

PROCEEDINGS  
OF THE  
INDIAN NATIONAL SCIENCE ACADEMY

(Formerly NATIONAL INSTITUTE OF SCIENCES OF INDIA)

PART A

PHYSICAL SCIENCES

No 5

September 1970

Vol 36



INDIAN NATIONAL SCIENCE ACADEMY  
NEW DELHI

*Price : Rupees Five and Twenty Paise*

P 272

Issued 12 February 1971



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In this issue of the Proceedings, we are publishing the papers presented at the Symposium on the Geology and Mineralogy of Atomic Mineral Deposits and Their Development for Use in the Nuclear Power Programme in India, held in New Delhi on 14-16 October 1968, under the auspices of INSA, Convener Professor D. N. Wadia. The usual procedure followed in accepting papers is on the basis of the recommendations of the referee.







# STUDIES IN THE BENEFICIATION OF URANIUM MINERALS FROM NARWAPAHAR—SINGHBHUM

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(Received 29 April 1969)

The low grade uranium deposit in Narwapahar in the Singhbhum Thrust Zone is likely to be an important source of uranium ore in view of its enormous reserve and favourable location. The mineralogical composition of the ore is as follows:

Quartz—51.0%,	Chlorite—38.0%,	Apatite—4.8%,
Magnetite—4.3%,	Sulphides—0.2%,	U <sub>3</sub> O <sub>8</sub> —0.055%.

The principal uranium mineral is uraninite, which is liberated mostly at about 270 mesh. The ore was wet ground (85%—200 mesh) and then hydraulically classified to three fractions, and the different fractions were wet tumbled. The tailings of all the fractions were retumbled. The retumbled tailings of the coarsest fraction were reground and tumbled. The combined concentrate (45.8%) assayed 0.1% U<sub>3</sub>O<sub>8</sub> eq., the recovery being 86.6%.

## INTRODUCTION

India has large resources of low grade uranium ores. The chlorite-sericite schists of Narwapahar area, Singhbhum District, Bihar, are among the important ones. Mineral beneficiation is expected to play an important role in upgrading of these ores.

The present investigation is on an ore sample from Narwapahar region in the Singhbhum Thrust Zone. The ore is a hydrothermal disseminated deposit, uraninite being deposited mostly as fine grains. The uranium mineral is associated mostly with apatite, magnetite and chlorite and it is liberated at very fine size ranges. The mineralogical composition of the sample is as given in Table I.

TABLE I  
*Mineralogical Composition of Narwapahar Ore*

Mineral	Wt. %	Mineral	Wt. %	Mineral	Wt. %
Quartz	51.0	Other transparent minerals	1.0	Pyrite	0.07
Chlorite	38.0	Magnetite	4.3	Other sulphides (Millerite, Pentlandite, Pyrrhotite and Molybdenite)	0.03
Apatite	4.8	Other oxides	0.7		
Tourmaline	Tr.	Chalcopyrite	0.1	Native Gold	Tr.



The radiometric assay of the ore is about 0.055%  $U_3O_8$  eq. Only a negligible amount (0.3%) of the total activity is due to thorium.

### EXPERIMENTAL

The ore is fine grained; the roll-crushed product (all — 10 mesh size) itself contains 11.9 per cent by weight of — 200 mesh size. In — 200 mesh size fractions all minerals are liberated. In any grinding operation most of the liberated uraninites are reported in the fine fractions, i.e. — 270 mesh size.

The amenability of the above ore to gravity concentration by wet tabling was studied. At first a series of three experiments were conducted with 3 kg. charge each time with different degrees of fineness in grinding. The grinding was done in a laboratory rod mill with a pulp of 66 per cent solids by weight. The ground product was directly tabled on a laboratory Deister table. Distinct bands of opaques, apatite, chlorite and quartz were formed on the table and a concentrate cut was taken up to the middle of apatite band each time. In case of finer feed the band spread was wider and hence the collection was more. The results of the above experiments are given in Table II.

TABLE II  
*Results of tabling with different amount of grinding*

Experiment No.	— 200 mesh fraction weight %	Concentrate weight %	$U_3O_8$ % equivalent	Distribution %
1	72.9	5.3	0.339	34.2
2	82.9	6.2	0.325	37.2
3	91.2	14.4	0.238	56.4

The above results clearly indicate that the recovery increases with degree of fineness in grinding, though there is fall in grade of the concentrate.

To study the effect of classification, a similar charge as in experiment No. 2 was classified into three fractions manually and each fraction was tabled separately on the laboratory Deister table. The result of this experiment is given in Table III, with that of experiment No. 2 for comparison.

This clearly shows that better recovery can be achieved by classification but the grade of concentrate will be lower.

Based on the above findings two more experiments were conducted to study in detail the behaviour of the ore on a wet table.

The first experiment was conducted with a charge of 15 kg. roll-crushed ore. The ore was ground by batches in a laboratory rod mill with a grinding pulp of 66 per cent solids by weight. The sieve analysis of ground product with respective assay and distribution figures is given in Table IV.



The ground product was classified into three fractions in a laboratory hydraulic classifier. The first fraction consisted mostly of +200 mesh size, the second fraction was mostly between -200 and 270 mesh size and the third fraction consisted mostly of -270 mesh size. Each of these fractions was wet tabled in a laboratory Deister table to collect concentrates ( $C_1$ ). The table tailings from first fraction were subjected to a light grinding operation and

TABLE III

*Effect of classification on tabling of Narwapahar Ore*

Experiment No.	- 200 mesh fraction weight %	Concentrate weight %	$U_3O_8$ % equivalent	Distribution%
2	(unclassified feed) .. 82.9	6.2	0.325	37.2
4	(classified feed) 82.9	12.0	<div> <div> Frac. 1:7.5 0.268  Frac. 2:2.9 0.210  Frac. 3:1.6 0.153 </div> <div> Average grade  = 0.239 </div> </div>	36.2 51.5 10.9 4.4

TABLE IV

*Sieve analysis of rod mill ground product*

Size fraction	Weight %	$U_3O_8$ % equivalent	Distribution %
+48	0.4	0.034	0.2
-48+65	0.9	0.034	0.6
-65+100	5.0	0.033	2.8
-100+150	9.7	0.034	5.7
-150+200	11.1	0.038	7.4
-200+270	17.9	0.047	14.5
-270	55.0	0.072	68.8
Calculated feed	100.0	0.058	100.0

tabled once more to collect concentrate ( $C_2$ ). The tailings of second and third fractions were also subjected to retabling separately, but without any further grinding, to collect concentrates ( $C_2$ ). The retabling operations were done to improve upon the recovery consequently lowering the assay of the tailings. The result of the experiment is given in Table V.

If the products with serial numbers 1, 2, 6, 7, 8, 10 and 11 are mixed a concentrate assaying 0.167 per cent  $U_3O_8$  equivalent with a recovery of 68.6 per cent may be obtained, collecting only 21.96 per cent of feed weight.



TABLE V  
Results of wet tabling of classified feed

Classified fraction No.	Serial No.	Table products	Weight %	U <sub>3</sub> O <sub>8</sub> % equivalent	Distribution %
Fraction 1	1	Conc. (C <sub>1</sub> )	4.46	0.165	13.8
	2	Conc. (C <sub>2</sub> )	0.48	0.346	3.1
	3	Middlings	2.39	0.026	1.2
	4	Tailings	12.76	0.019	4.5
	5	Slimes	2.91	0.032	1.7
			23.00	0.0565	24.3
Fraction 2	6	Conc. (C <sub>1</sub> )	5.18	0.253	24.6
	7	Conc. (C <sub>2</sub> )	0.87	0.067	1.1
	8	Middlings	5.15	0.070	6.8
	9	Tailings	19.30	0.015	5.4
			30.50	0.0674	37.9
Fraction 3	10	Conc. (C <sub>1</sub> )	4.65	0.195	17.0
	11	Conc. (C <sub>2</sub> )	1.17	0.099	2.2
	12	Middlings	4.78	0.025	2.2
	13	Tailings	35.90	0.025	16.4
			46.50	0.0435	37.8
Feed			100.00	0.0534	100.0

The next experiment was done with a charge of 18 kg. of ore ground finer than the feed in previous experiment. The sieve analysis of the ground product is given in Table VI.

TABLE VI

Mesh size	Weight %	U <sub>3</sub> O <sub>8</sub> % equivalent	Distribution %
+48	0.1	0.026	Tr.
-48+65	0.2	0.026	0.1
-65+100	2.0	0.026	0.9
-100+150	4.0	0.022	1.7
-150+200	8.0	0.026	3.5
-200+270	19.5	0.041	13.6
-270	65.8	0.068	80.2



TABLE VII  
*Size distribution in classified products*

Mesh size	Weight per cent in		
	Fraction 1	Fraction 2	Fraction 3
48	0.5	Tr.	—
—48+65	1.0	Tr.	—
—65+100	9.0	0.5	Tr.
—100+150	17.5	1.0	Tr.
—150+200	20.4	8.9	3.0
—200+270	37.2	27.5	7.5
—270+325	9.4	40.1	30.5
—325+400	5.0	15.5	23.3
—400	Tr.	6.5	35.7

TABLE VIII

Classified fraction	Serial No.	Table products	Weight %	U <sub>3</sub> O <sub>8</sub> % eq.	Distribution %
Fraction 1	1	Conc. (C <sub>1</sub> )	3.46	0.349	22.5
	2	Conc. (C <sub>2</sub> )	0.54	0.103	1.0
	3	Conc. (C <sub>3</sub> )	0.62	0.118	1.4
	4	Conc. (C <sub>4</sub> )	0.54	0.052	0.5
	5	Middlings	1.68	0.011	0.4
	6	Tailings	10.32	0.014	2.7
	7	Slimes 1	1.18	0.049	0.9
	8	Slimes 2	3.16	0.022	1.3
			21.50	0.077	30.7
Fraction 2	9	Conc. (C <sub>1</sub> )	2.88	0.275	14.7
	10	Conc. (C <sub>2</sub> )	0.68	0.105	1.3
	11	Middlings	5.07	0.013	1.2
	12	Tailings	14.05	0.017	4.4
	13	Slimes	5.52	0.029	3.0
			28.20	0.058	24.6
Fraction 3	14	Conc. (C <sub>1</sub> )	2.01	0.473	17.7
	15	Conc. (C <sub>2</sub> )	1.04	0.115	2.2
	16	Middling 1	7.65	0.055	7.8
	17	Middling 2	2.74	0.012	0.6
	18	Tailings	20.33	0.011	4.1
	19	Slimes 1	10.98	0.047	9.6
	20	Slimes 2	5.55	0.026	2.7
			50.30	0.048	44.7
Feed			100.00	0.054	100.00



The ground charge was subjected to hydraulic classification to collect three classified fractions. Sieve analysis of these fractions were as shown in Table VII.

Each of the three fractions was wet tabled in a laboratory Deister table to collect concentrate ( $C_1$ ). The tailings were retabled in all the cases to produce another concentrate ( $C_2$ ). The tailings and middlings obtained after the retabling of first fraction were given a light grinding and then treated on the table twice in a similar manner to collect concentrates ( $C_3$  and  $C_4$ ). The results of experiment are given in Table VIII.

The fractions with serial numbers 1, 2, 3, 4, 7, 9, 10, 14, 15, 16 and 19 when combined will give a grade of 0.136 per cent  $U_3O_8$  eq. with a recovery of 79.6 per cent and the concentrate weight will be 31.58 per cent of feed. If the slime fractions numbering 8, 13 and 20 are also added to the concentrate the recovery increases to 86.6 per cent with a grade of 0.1 per cent and the weight collected will be 45.81 per cent of the feed.

#### CONCLUSION

It will be thus seen that low grade uranium ore from Narwapahar region can be upgraded by wet tabling of finely ground ore after hydraulic classification. Since the material is finely disseminated no other gravity process appears suitable.

#### ACKNOWLEDGEMENTS

The authors are thankful to late Dr. D. N. Wadia for making the ore sample available for the present investigation and to Dr. V. K. Moorthy, Head, Metallurgy Division, B.A.R.C., Bombay, for his keen interest in the present studies.



SOME RESULTS OF LIXIVIATION TESTS ON BULK  
URANIFEROUS QUARTZITE ORE UNDER FIELD  
CONDITIONS AT CHHINJRA, KULU DISTRICT,  
HIMACHAL PRADESH

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Uraninite occurs as veins in a hard, compact quartzite at Chhinjra in the Middle Himalayas described by Dar (1964). As the size of the deposit does not warrant, at this stage, the setting up of a conventional mill for uranium extraction, two tests on bulk ore were carried out at site under field conditions, after a study of suitable parameters in the laboratory, to extract uranium cheaply by lixiviation methods which are the only methods suitable for deposits of such size in such locations. Here, however, the first difficulty which had to be overcome was to reduce grinding of the ore to the barest minimum—a contingency which does not arise in the case of pervious sandstone type deposits. The other parameters involved in the study were pH and redox potential levels required to be maintained during leaching, control of iron present which affects oxidation of tetravalent uranium to the soluble hexavalent state, and peptization problems in precipitation of uranium from pregnant liquor.

The parameters found suitable in the laboratory yielded better results in bulk treatment of ore in the field. In the field test No. 2, at a feed size of —10 mesh, with 70 lb/ton of 1 per cent  $H_2SO_4$  and 10 lb/ton  $MnO_2$ , a leachability of 83.3 per cent was obtained, from ore analysing 0.06 per cent  $U_3O_8$ , against 67.9 per cent leachability obtained in the laboratory tests with 60 lb/ton of 1 per cent  $H_2SO_4$  and 10 lb/ton of  $MnO_2$  on an ore analysing 0.10 per cent  $U_3O_8$ . Although good results have emerged from this work, investigations are now being carried out to reduce acid and oxidant consumption, by controlling ferrous/ferric ratios, and peptization losses.

#### INTRODUCTION

The main problem in treating ore from comparatively small deposits in out-of-the-way places is reduction of cost by adoption of methods and improvisation of equipment which would make the cost of the product fairly competitive.

Uraninite occurs in the Chhinjra quartzite as veins or veinlets and as paint or coatings, as well as replacement of quartz grains. Occasionally, secondary uranium minerals are also present. Other associates of the ore are copper sulphides, pyrite, magnetite, etc. The quartzite ore is hard and compact necessitating grinding which is not necessary in the sandstone type deposits the porosity of which facilitates complete acid attack.

Tests in the laboratory showed that physical beneficiation is not suitable as reasonable recoveries could be obtained only at a grind of 75 per cent —200 mesh (ASTM). Such a fine grinding entailed increase in the over-all



cost of operation, recovery of 70 per cent in the concentrate with a recovery of 90 per cent or so of uranium in leach liquor would have meant an over-all recovery of 63 per cent only. This method has, therefore, to be discarded.

Agitation leaching tests at 80 per cent —200 mesh yielded recoveries of 97 per cent in 12 hours with 80 lb/s. ton  $H_2SO_4$  and 11.2 lb/s. ton  $MnO_2$  at a pH of 1.5 and redox potential of —480, but was given up as it involved not only fine grinding of ore and high acid and oxidant consumption but introduced additional expenditure on account of energy required for agitation and equipment required for conventional leaching.

#### EXPERIMENTAL

Out of a number of percolation leaching, static leaching and pugging tests carried out in the laboratory, percolation leaching was found to be the cheaper and more suitable method for field conditions.

The most suitable parameters for extraction of uranium in the laboratory were 60 lb/s. ton of 1 per cent  $H_2SO_4$  and 10 lb/s. ton of  $MnO_2$  for obtaining a recovery of 68 per cent in 35 days of circulation from ore analysing 0.10 per cent  $U_3O_8$  at —10 mesh (ASTM).

#### Field tests

Following a series of laboratory tests (discussed separately by Jayaram *et al.* 1970) to ascertain the most suitable parameters for feed size, acid strength, time, amount of oxidant required to maintain redox potential at the required level of —430 m for conversion of iron from ferrous to ferric state and uranium from tetravalent to hexavalent state, control of pH for dissolution of uranium and peptization problems in uranium precipitation with NaOH, two tests were carried out on bulk ore weighing 6.5 s. tons and 10 s. tons analysing 0.142 per cent and 0.06 per cent  $U_3O_8$ , respectively.

The field tests were carried out close to a water source in the prospecting area at Chhinjra on the Bhuntar-Manikaran road.

#### Construction of Platforms

Three platforms, 20 ft.  $\times$  15 ft. in area, were prepared. The second platform from the top one was 8 ft. below it and the third 6 ft. below the second. Each platform was lined with a 1-inch thick cement-concrete layer. The middle platform was coated with 1/8-inch thick coal-tar layer and lined with a polythene sheet. Two tanks of 4,500 litres capacity for acid and leach liquor fabricated at site, with locally available wooden planks supported by 1½-inch angle-iron framework, were coated inside with a 1/8-inch thick coal-tar layer followed by polythene sheet lining. The tank on the uppermost platform was used for acid, that on the lowest platform for collection of leach liquor. The central platform on which the ore was spread had a gentle slope of 1 in 200 for the leach liquor to gradually drain off into the lowest tank.



*Crushing*

The ore received at a size of 1 to 1½-inch was jaw-crushed and then roll-crushed in crushers of 2 tons/day capacity to 10 mesh (ASTM) size (13.08 per cent and 30.0 per cent oversize) respectively in respect of test Nos. 1 and 2.

*Percolation*

The crushed ore was spread in 1-ft. thick layer over a 2-inch thick filter-bed made up of ¾-inch to 1/2-inch fragments of gangue on the middle platform. Acid from the acid tank was passed through 3 polythene pipes at 3.5 lit/mt/60 sq. ft. and was sprayed on the stack evenly to prevent its channelization. Leach liquor after percolation was passed through an asphalted wooden chute into the lowest tank. The leach liquor was pumped back into the acid tank and recirculated through the ore stack for 8 hours every day leaving 16 hours per day for curing till maximum loading of uranium was obtained when it was withdrawn and uranium precipitated. During the precipitation and filtration of each batch which took more than 48 hours additional curing time was given before circulation of fresh acid. The results of these tests are given in Tables I and II and Fig. 1.

TABLE I

Tons treated: 6.5 s. tons	Residue: 0.025% $U_3O_8$	Leachability: 76.86%
Stack height: 1 foot	Acid used: 100 lb/s. ton 1% v/v $H_2SO_4$	Recovery: 65.78%
Feed assay: 0.142% $U_3O_8$	Size: 10 mesh (ASTM) 13.08% oversize	End pH: 2.0 (by paper)

S. No.	Stage No.	No. of days	Leach liquor data			Estimated leachability % over-all	Cake collected	
			Volume (litres)	G/lit/solids (sodium cake)	Mg/lit $U_3O_8$		Grade % $U_3O_8$	% Recovery
1	I	3	1687	6.00	792	16.00	13.22	15.90
2	Curing	2	—	—	—	—	—	—
3	II	2	1545	8.40	1646	30.37	19.65	24.59
4	Curing	2	—	—	—	—	—	—
5	III	1	3210	0.75	220	—	—	—
		2	—	1.01	326	—	—	—
		3	2109	1.80	387	—	—	—
		4	2109	2.64	364	9.22	13.85	8.30
6	Curing	2	—	—	—	—	—	—
7	IV	3	1194	3.14	659	9.40	20.00	7.38
8	Curing	2	—	—	—	—	—	—
9	V	1	1605	1.50	455	—	—	—
		2	—	2.00	469	—	—	—
		3	1333	2.60	457	7.27	17.50	6.24
10	Curing	2	—	—	—	—	—	—
11	VI	1	776	1.35	314	2.90	20.3	2.40
12	Curing	2	—	—	—	—	—	—
13	VII	1	775	1.10	160	1.40	8.8	0.71



*Precipitation*

Uranium in the pregnant liquor thus obtained was precipitated with sodium hydroxide at a pH of 10.5 as crude cake which after filtration was dried at the ambient temperature. On analysis of this cake, it was found that the uranium recovered in it accounted for only 65.78 and 58.03 per cent of the uranium in the pregnant liquor in which a leachability of 76.86 and 83.33 per cent respectively from the ore had been affected. There

TABLE II

Tons treated: 10.0 s. tons	Acid used: 70 lb/ton of 1% v/v $H_2SO_4$	Recovery: 58.03%
Size: 10 mesh (ASTM) 30% oversize	Feed assay: 0.06% $U_3O_8$	Oxidant: 10 lb/ton $MnO_2$
	Leachability: 83.33%	Residue assay: 0.01% $U_3O_8$

Sl. No.	Stage No.	No. of days	Volume of leach liquor litres	Leach liquor data		Estimated leachability % over-all	Cake collected	
				G/lit sodium cake	Mg/lit $U_3O_8$		Grade % $U_3O_8$	Recovery
1	I	4	2300	7.00	400	16.6	5.0	13.75
2	Curing	13	—	—	—	—	—	—
3	II	4	2375	7.06	300	13.3	3.5	12.16
4	Curing	6	—	—	—	—	—	—
5	III	4	2450	5.00	290	11.1	3.17	5.80
6	Curing	5	—	—	—	—	—	—
7	IV	4	2450	6.50	410	18.3	3.40	12.90
8	Curing	13	—	—	—	—	—	—
9	V	4	2200	6.00	370	15.0	3.25	11.25
10	Curing	9	—	—	—	—	—	—
11	VI	3	2000	3.60	150	5.8	2.00	0.92
12	Curing	3	—	—	—	—	—	—
13	VII	3	700	1.80	230	3.0	2.00	1.25

was thus a loss of 11.08 and 25.3 per cent uranium, respectively, during precipitation. Tests carried out on this problem (Table III) showed that on the average about 23.3 per cent uranium could not be precipitated with NaOH (commercial) due to peptization and carbonate complexing.

Experiments carried out to ascertain the pH level at which minimum loss occurred showed that at a pH of 10.5 the loss was reduced to 9.5 per cent from 23.3 per cent (Table IV).



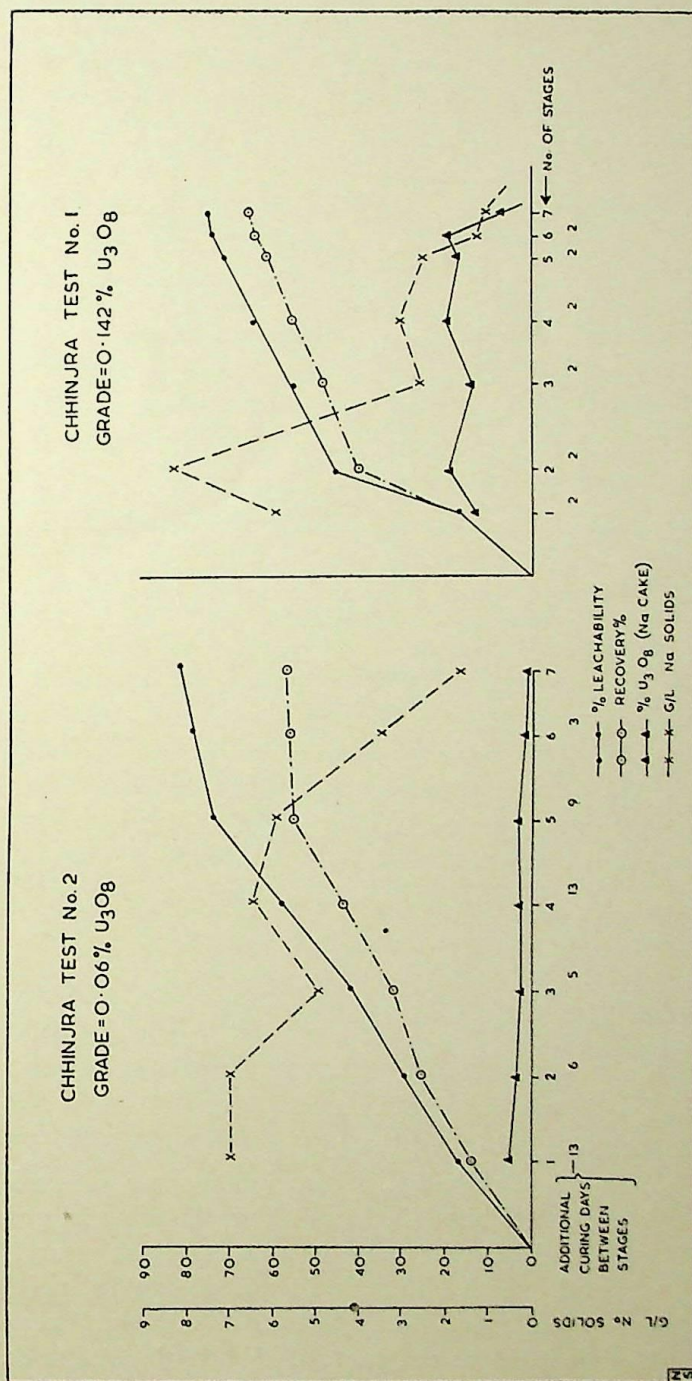


FIG. 1



TABLE III  
Precipitation tests on cold leach liquors. pH of precipitation: 10.5

Sl. No.	Precipitate 1 with NaOH (Com.) from cold leach liquor (in gm)	Precipitate 2 from filtrate in col. 2 after boiling with HNO <sub>3</sub> (in gm)	Per cent U in precipitate 2 (filtrate of 1)	Per cent U in precipitate 1
1	2	3	4	5
1	0.1840	0.0482	20.75	79.25
2	0.2772	0.0984	26.20	73.80
3	0.2315	0.0714	23.6	76.40
4	0.1764	0.0490	21.3	78.7
5	0.0030	0.0011	27.0	73.0
6	0.0172	0.0053	21.0	79.0
Average:			23.3	

TABLE IV  
Precipitation at different pH

S. No.	Precipitation pH	Per cent losses in filtrate
1	3.5	99.2
2	4.0	98.0
3	4.5	88.0
4	9.5	32.1
5	10.0	17.9
6	10.5	9.5
7	11.0	17.6
8	11.5	84.2
9	12.0	70.9
10	> 12.0	90.0

#### CONCLUSIONS

The foregoing data show that:

1. With the distribution of uranium in various sized fractions being generally of the same order, the material ground to 10 mesh (ASTM) size would be as well as that ground further to any other size. Though increased specific surface due to fine grinding facilitates better acid attack, percolation was hindered due to compaction. When the size is coarser, the diffusion of acid is low due to the impermeability and precipitation of sulphates and hydroxides on the ore grains.



2. For ore of a given tenor, there is an optimum concentration of solids at which the highest recovery of uranium is obtainable beyond this point the leachability of uranium decreases at the expense of other elements like iron which increases with a decrease in pH. This is due to the reduction and reprecipitation of ferric iron and uranium being leached in the top layers when they come into contact with pyrite and other ferrous minerals, in the bottom layers of the stack. (Please refer to Table I, S. Nos. 5 and 9).
3. The loss in precipitation in addition to handling losses is due to (i) the carbonate complexing with the high amount of  $\text{Na}_2\text{CO}_3$  present (15 per cent  $\text{Na}_2\text{CO}_3$  present in the commercial NaOH used in the field), (ii) low concentrations of uranium in leach liquors, (iii) complexing of uranium hydroxide with ferric hydroxide which is a suspensoid and consequent loss during filtration.

While a breakthrough for leaching uranium from an impervious hard rock, located in out-of-the-way places, has been made, additional work is now necessary for further cost reduction. This work will involve theoretical studies on the adsorption process, porosity and effect of bacterial leaching. Experiments have already been initiated for recovering uranium by using amberlite-IRA-400 resin and precipitating uranium with NaOH. This method has the advantage of low water consumption, production of very few effluents, and not much skilled supervision after the process has been set, all of which sectors contribute to reduction in the cost of initial investment and cost of uranium recovery.

#### ACKNOWLEDGEMENTS

The authors are thankful to the late Dr. D. N. Wadia, F.R.S., former Geological Adviser to the Government of India, for the keen interest he has evinced in this investigation. We are particularly grateful to Shri K. K. Dar, Regional Director (B), but for whose imagination, guidance and persistence this work would not have been possible.

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# LEACHING AND PRECIPITATION OF URANIUM FROM QUARTZITE ORES AT CHHINJRA, KULU DISTRICT, HIMACHAL PRADESH

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(Received 29 April 1969)

The lixiviation of uranium ore occurring in a quartzite at Chhinjra presented certain problems from the grinding stage to the final precipitation of uranium as crude cake at site as cheaply as possible without use of conventional plant. Experiments were carried out to find suitable parameters for feed size, pH, redox potential, and the like. It was found that -10 mesh (A.S.T.M.) feed size provided a via media between too coarse a size, which reduced recovery, and too fine a size which resulted in compaction of ore and prevented acid percolation.

Leaching efficiency, which depends largely on the oxidation of uranium to a higher valance state, was found to increase with the use of  $\text{MnO}_2$ , or  $\text{HClO}_4$ , but there were significant losses in the precipitate due to occlusion of uranium with ferric ion. Reduction of the ferric to ferrous ion, which thus became necessary, was effected by addition of scrap iron or zinc to the pregnant liquor before precipitation which resulted in an increase in precipitation of uranium from it.

The effects of oxidation on leaching and precipitation of uranium are discussed.

## INTRODUCTION

Use of lixiviation or heap leaching of uranium for low-grade ores situated far from mills or high-grade ores in small deposits for which conventional plants cannot be set up is becoming increasingly important. The Chhinjra uranium ore generally provides three grades: (i) Low grade (up to 0.10 per cent  $\text{U}_3\text{O}_8$ ), (ii) medium grade (0.11 to 0.2 per cent  $\text{U}_3\text{O}_8$ ) and (iii) high grade (above 0.21 per cent  $\text{U}_3\text{O}_8$ ). Unlike uranium occurrences in the porous and friable sandstone type deposits, which are eminently suited for such treatment, uranium in Chhinjra occurs in a hard, compact, impermeable rock-like quartzite with which are associated pyrite (2.3 per cent), Cu-sulphides (0.5 to 1.0 per cent), other iron minerals like magnetite, hematite, etc., and presents problems peculiar to itself for treatment by this process.

Although leaching experiments carried out in laboratory on ores from Kulu Himalayas showed that use of oxidants increased the leachability of uranium and reduced acid consumption considerably, in tests on bulk ore at site it was found that 23 per cent of uranium leached escaped precipitation with commercial NaOH resulting in loss in recovery. Investigation of this in the laboratory indicated that the reason for this loss was the occlusion of



uranium in the ferric iron, and its reduction to ferrous iron by scrap iron or zinc to be a useful remedial measure.

The results of these laboratory investigations which will now be utilized in the field operations are also presented.

#### LEACHING

One per cent V/V  $\text{H}_2\text{SO}_4$  was percolated for eight hours through 1-ft. high stacks of -10 mesh ore with which was admixed an oxidant in varying quantities, all held in perspex columns. The initial leach liquor obtained was recirculated after 16 hours of curing, through the column till optimum loading of uranium in it was attained.

Table I shows that with 5 lb/ton  $\text{HClO}_4$  and 40 lb/ton of 1 per cent  $\text{H}_2\text{SO}_4$ , the  $\text{Fe}_2 : \text{Fe}_3$  ratio rises from 1 : 0.6 to 1 : 16 in contact time of 72 hours, leachability increases from 2.8 to 16.5 per cent.

TABLE I  
*Leaching accompanied by oxidation with  $\text{HClO}_4$*

Code No. CH/11		Feed assay: 0.42% $\text{U}_3\text{O}_8$		Size: -10 mesh		
Sl. No.	Days No.	$\text{H}_2\text{SO}_4$ used lb/ton	Percentage strength of acid	$\text{HClO}_4$ lb/ton	$\text{Fe}_2 : \text{Fe}_3$	Percentage leachability
1	1	40	1	—	1 : 1	4.4
2	2	40	1	—	1 : 0.4	4.0
3	3	40	1	—	1 : 0.6	2.8
4	1	40	1	5.0	1 : 18	10.0
5	2	40	1	5.0	1 : 16	7.5
6	3	40	1	5.0	1 : 16	16.5

Table II shows that with similar quantity and strength of  $\text{H}_2\text{SO}_4$  and with the addition of 5 lb/ton  $\text{MnO}_2$ , the  $\text{Fe}_2 : \text{Fe}_3$  ratio rises from 1 : 0.20 to 1 : 0.55 in a period of 4 days, with improvement in leachability from 9.7 per cent without the use of  $\text{MnO}_2$  to 17.1 per cent.

In the other set of tests using 15 lb/ton  $\text{MnO}_2$  and the same quantity and strength of  $\text{H}_2\text{SO}_4$ , the ferrous : ferric ratio rises from 1 : 0.20 to 1 : 8.00 with improvement in leachability from 9.7 per cent to 58.10 per cent in a time of 17 days. It is significant that in these tests, highest recovery of 65.06 per cent is obtained with 30 lb/ton of 1 per cent  $\text{H}_2\text{SO}_4$  and 15 lb/ton of  $\text{MnO}_2$  at a  $\text{Fe}_2 : \text{Fe}_3$  ratio of 1 : 4.80 in 7 days and that with further increase in contact time leachability is reduced progressively to 50.93 per cent. This is due to the increased ferric iron, coming in contact with iron in the ore and consequent precipitation of uranium, after reduction.



TABLE II

*Leaching accompanied by oxidation with MnO<sub>2</sub>*

Feed size: -10 mesh

Feed assay: 0.11% U<sub>3</sub>O<sub>8</sub>

Sl. No.	No. of days	H <sub>2</sub> SO <sub>4</sub> used		pH	MnO <sub>2</sub> used lb/ton	Fe <sub>2</sub> : Fe <sub>3</sub>	U : Fe <sub>3</sub>	Percentage leachability
		lb/ton	Percent-age strength					
1	4	40	1	0.65	Nil	1 : 0.20	—	9.7
2	1	40	1	0.65	5	1 : 0.33	2.2	15.0
3	2	40	1	0.60	5	1 : 0.41	0.2	25.0
4	4	40	1	0.55	5	1 : 0.55	2.5	17.1
5	1	40	1	0.7	15	1 : 2.50	1 : 1.6	41.3
6	2	40	1	0.7	15	1 : 8.00	1 : 2.0	58.1
7	3	40	1	0.7	15	1 : 9.8	1 : 2.1	53.4
8	1	30	1	0.57	15	1 : 2.65	1 : 4.5	14.52
9	3	30	1	1.0	15	1 : 2.70	1 : 4.7	18.70
10	5	30	1	1.2	15	1 : 3.60	1 : 2.4	41.60
11	7	30	1	1.1	15	1 : 4.80	1 : 1.8	65.06
12	13	30	1	1.2	15	1 : 5.30	1 : 1.9	50.43

## PRECIPITATION

The leach liquor obtained at the end of each test was split into three parts, one part for direct precipitation of uranium, the second for reduction with zinc followed by precipitation, and the third for reduction with scrap iron prior to precipitation. In all these cases, the leach liquors, the filtrates,

TABLE III

*Precipitation pH and losses of uranium in filtrate*

Sl. No.	Precipitation pH	Percentage losses in filtrate
1	3.5	99.2
2	4.0	98.0
3	4.5	88.0
4	9.5	32.1
5	10.5	17.9
6	10.5	9.5
7	11.0	17.6
8	11.5	84.2
9	12.0	70.9
10	12.0	90.0



TABLE IV  
Stage precipitation with different reagents

Leach liquor data							Precipitation data							Cake data					Filtrate data				
Sl. No.	Vol. in c.c.	pH	-mv	Fe <sub>2</sub> : Fe <sub>3</sub>	U <sub>3</sub> O <sub>8</sub> mg/l	U <sub>3</sub> O <sub>8</sub> total mg.	Re-agent	pH	EH	Fe <sub>2</sub> : Fe <sub>3</sub>	Precipitating agent	pH	-mv	Wt. gm.	gm. % U <sub>3</sub> O <sub>8</sub>	Total U <sub>3</sub> O <sub>8</sub> /mg	Percentage dist.	Vol.	pH	-mv	Fe <sub>2</sub> : Fe <sub>3</sub>	U <sub>3</sub> O <sub>8</sub> mg/l	Percentage dist.
1	250	1.75	-450	1 : 8	730	183	-	-	-	-	NaOH	10.5	+50	2.700	6.30	170	95.25	100	8.6	-140	1 : 2	87	4.75
2	250	1.75	-450	1 : 8	730	183	-	-	-	-	NH <sub>4</sub> OH	10.5	+210	0.906	19.60	177	96.79	100	8.6	-120	1 : 2	60	3.31
3	100	1.75	-450	1 : 8	730	73	Zn	4.4	-220	1 : 0.25	NaOH	10.5	+120	0.669	25.10	72	98.9	100	9.5	+85	1 : 0.7	20	1.1
4	100	1.75	-450	1 : 8	730	73	Zn	4.4	-220	1 : 0.25	NH <sub>4</sub> OH	10.5	+50	0.450	40.70	72	100.00	100	10.3	+215	1 : 0.5	Nil	-
5	100	1.75	-450	1 : 8	730	73	Scrap iron	2.5	-290	1 : 0.40	NaOH	10.5	+40	0.720	10.00	72	98.5	200	9.4	+220	1 : 1	14.5	1.5
6	100	1.75	-450	1 : 8	730	73	„	2.5	-290	1 : 0.40	NH <sub>4</sub> OH	10.5	+80	0.490	14.90	73	99.7	150	10.0	+50	1 : 0.7	4.0	0.32
7	250	∠ 2.0	-650	1 : 7	730	183	„	5.4	+80	-	NaOH	10.5	+125	0.602	29.9	180	100.00	200	10.2	+60	Fe <sub>2</sub>	-	-
8	300	1.12	-530	1 : 5.4	760	228	-	-	-	-	NaOH	16.5	+150	3.5	6.0	210	92.1	450	10.0	-	-	40	7.8
9	250	1.20	-	1 : 8.4	1310	327	-	-	-	-	Ca(OH) <sub>2</sub>	12.0	+120	3.8	6.5	247	75.5	4000	12.0	-	-	16	19.6
10	600	2.0	-	1 : 6	866	520	-	-	-	-	Ca(OH) <sub>2</sub>	5.0	-	3.2	4.9	158	30.3	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	Ca(OH) <sub>2</sub>	9.0	-	4.1	11.87	287	55.2	700	9.0	-	-	47	6.3
12	400	∠ 2.0	-	1 : 9	425	170	-	-	-	-	NaOH	9.0	-	5.0	3.1	155	89.1	550	9.0	-	-	35	10.9
13	500	∠ 2.0	-	1 : 9	425	213	-	-	-	-	Ca(OH) <sub>2</sub>	3.0	-	10.0	0.23	23	11.26	650	-	-	-	72	21.6
	-	-	-	-	-	190	-	-	-	-	Ca(OH) <sub>2</sub>	9.0	-	11	1.3	143	67.10		-	-	-	5	22.7
14	100	∠ 2.0	-	-	22	2.2	-	-	-	-	Ca(OH) <sub>2</sub>	10.5	-	-	-	1.6	72.7	-	-	-	-	40.0	-
15	100	∠ 2.0	-	-	20	2.0	-	-	-	-	Ca(OH) <sub>2</sub>	3.5	-	-	-	0.2	10.0	-	-	-	-	-	-
16	85	∠ 2.0	-	-	-	1.8	-	-	-	-	NaOH	12.0	-	-	-	1.4	-	-	-	-	-	-	-
17	100	∠ 2.0	-	-	100	10	-	-	-	-	NaOH	10.5	-	-	-	6.0	60.0	-	-	-	-	40	40
18	100	∠ 2.0	-	-	100	10	-	-	-	-	NaOH	11.0	-	-	-	6.2	62.0	-	-	-	-	38	38
19	120	2.0	-	-	100	12	-	-	-	-	NaOH	11.5	-	-	-	8.8	73.3	-	-	-	-	32	26.6



Cake data

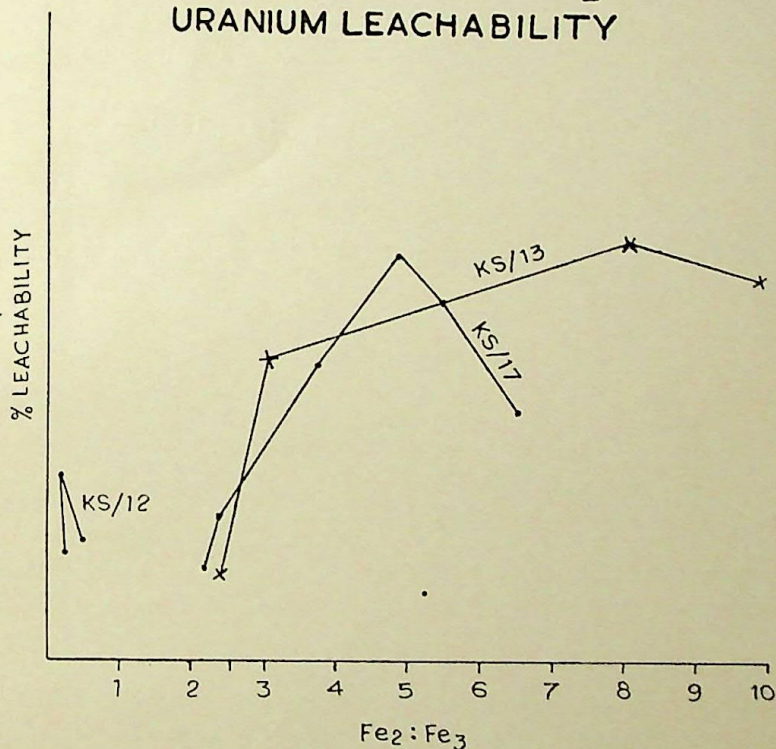
$U_3O_8$ mg/l	Percentage dist.	Wt. gm.	Percentage $U_3O_8$ grade	Percentage dist.	Remarks
Nil	Nil	57.00	6.07	99.8	Direct precipitation.
6.7	0.42	17.00	9.16	98.5	"
14.0	1.60	8.20	10.97	97.9	"
14.2	2.58	5.30	11.72	94.6	"
14.6	4.00	4.00	9.00	93.5	"
113	46.50	4.12	3.17	53.5	Field test stage III.
1293	40.40	-	-	59.5	Reduction with zinc granules 5 gm.
2900	93.20	-	-	7.0	
2636	70.60	-	-	29.4	
1727	38.90	-	-	61.1	*1 c.c. $H_2SO_4$ added for hastening reaction.
1737	37.10	2.36†	16.40	41.5	†Iron-Zinc-Uranium cement.
1.95	Nil	24.73	1.66	43.9	+ 20.5 per cent for analysis (total 104.90).
2475	75.1	-	-	20.4	
2812	81.3	-	-	18.7	
2636	70.6	-	-	29.4	
1462	32.9	-	-	67.1	*1 c.c. $H_2SO_4$ added.
3177	72.7	0.465	2.23	1.1	34.7 per cent for analysis: (324 mg).
0.55	Nil	45.36	1.30	63.1	Total 98.9 per cent (1.1 + 63.1 + 34.7).



and the cakes and the cements were analysed for  $U_3O_8$ ,  $Fe_2 : Fe_3$  ratio, and their  $pH$  and  $Eh$  found. The effect of different precipitants like  $NH_4(OH)$ ,  $NaOH$  and  $Ca(OH)_2$  was also studied. The results of these tests are summarized in Tables III, IV and V.

Table III shows the results of direct precipitation tests with commercial  $NaOH$  at different  $pH$ . A  $pH$  of 10.5 is found to be optimum for precipitation.

PLATE I. EFFECT OF  $MnO_2$  ON URANIUM LEACHABILITY



CODE NO	$MnO_2$ lbs/TON	$H_2SO_4$ lbs/TON
KS 12	5	40
KS 13	15	40
KS 17	15 •	30



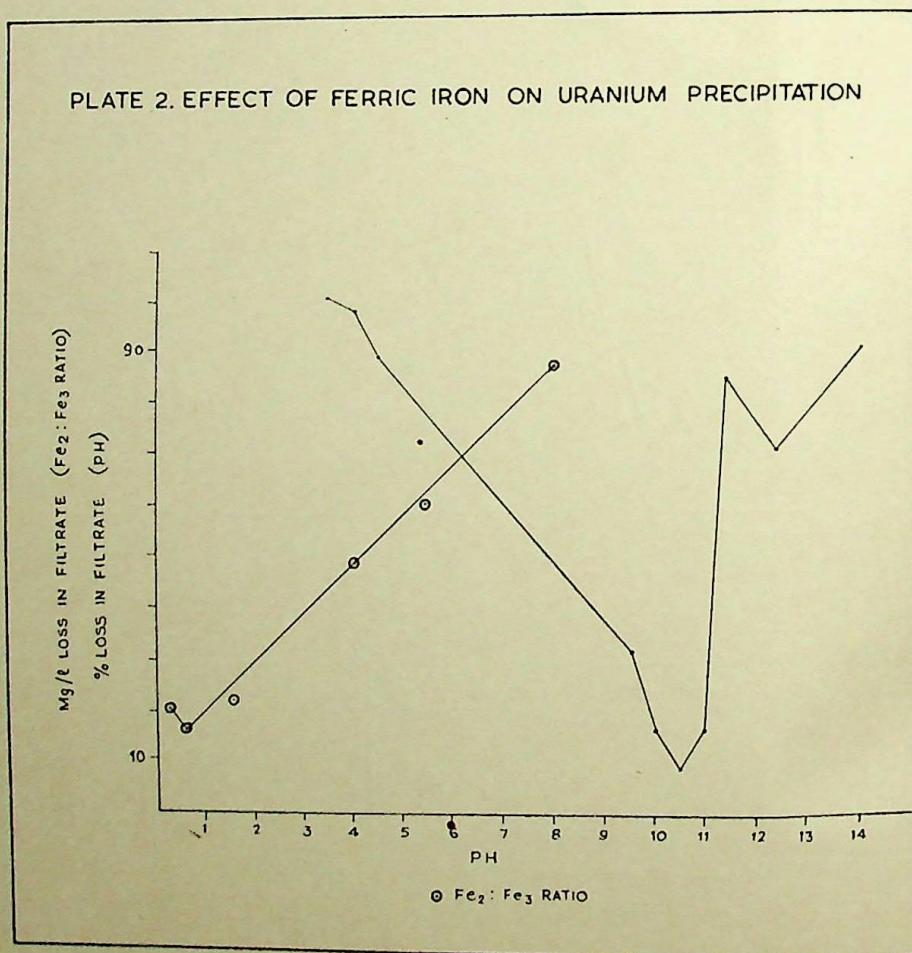
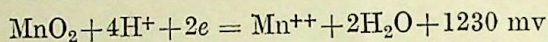
Table IV shows the effect of prereduction and stage precipitation on the loss of uranium in the filtrates, with different precipitating agents.  $\text{NH}_4\text{OH}$  is found to be the best precipitating agent.

Table V shows the effect of uranium concentration in the leach liquors on the loss of uranium as a suspensoid and the effect of various levels of reduction on the grade of the cake and cement precipitated.

#### CONCLUSIONS

The implications and results of these experiments may be summarized as follows:

1. Optimum leachability of uranium is obtained with 15.0 lb/ton of  $\text{MnO}_2$  due to the oxidation of tetravalent uranium to hexavalent uranium which is easily soluble in acid. The catalytic action involved may be written as:





The ferrous ion is thus oxidized to ferric state ( $E^\circ = -771$  mv) which in turn oxidizes the uranium. This is confirmed by Eh readings which show that maximum leaching of uranium is obtained at about  $-400$  mv (see graph, Plate 1, Tables I and II).

2. (i) A pH of 10.5 is found to be optimum for precipitating uranium with commercial NaOH (Table III and Plate 2).

(ii)  $\text{NH}_4\text{OH}$  is found to be a better precipitating reagent than NaOH or  $\text{Ca}(\text{OH})_2$  (Table IV).

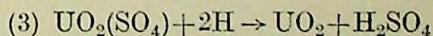
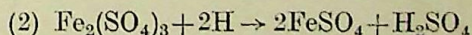
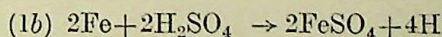
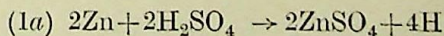
3. The loss in the filtrate is due to:

(i) The high amount (15 per cent) of  $\text{Na}_2\text{CO}_3$  present in the commercial NaOH due to which uranium in the leach liquor complexes with  $\text{Na}_2\text{CO}_3$  as a carbonate and escapes precipitation unless pH of 12 is maintained during precipitation. This in turn, however, increases the carbonate content in the liquor which leads to further complexing of uranium with  $\text{Na}_2\text{CO}_3$  (Table II and Sl. Nos. 11 and 12 of Table IV).

(ii) Peptization, as the leach liquors obtained in percolation leaching contained very low concentration of uranium, being 400 mg/litre and less (Table V, Sl. Nos. 1 to 6).

(iii) Oxidation during leaching results in the formation of excess ferric hydroxide during precipitation, which remains in a colloidal state during precipitation and the uranium hydroxide occluded in it escapes precipitation.

4. Controlled prereduction of the leach liquor with zinc reduces the uranium losses from 4.75 per cent to 1.1 per cent and with scrap iron to 1.5 per cent (please refer to Table IV, col. 24). This is due to the reduction of ferric ion to ferrous ion (cf. 5 and 6 with 12 and 13 of Table IV and Sl. Nos. 7 to 18 of Table V). The reduction reactions may be written as:

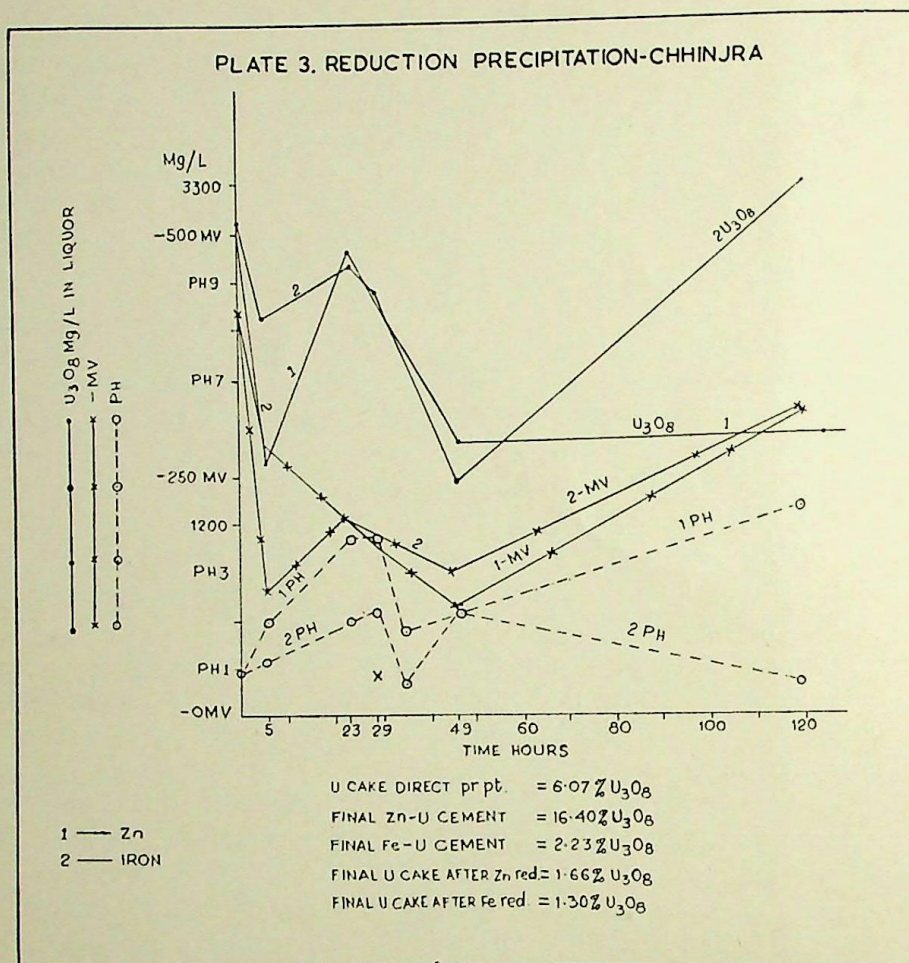


5. Complete reduction of the leach liquor, however, yielded a uranium cement (uranium oxy-sulphide) which, though richer in grade, requires subsequent cleaning steps.

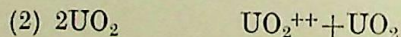
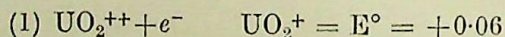
6. Post-reduction precipitation yielded a cake of higher grade of uranium with zinc than with iron (cf. Sl. No. 12 with 18, Table V).

7. The availability of Zn/Fe and the free  $\text{H}_2\text{SO}_4$  for starting the initial reaction represented by equations (1a) and (1b) determine the course of reduction (Plate 3).





8. The  $UO_2$  cement precipitated forms hydroxides depending upon the pH and the uranium concentrations of the leach liquor and when the time allowed for the reaction is large, the cement obtained gets redissolved. Auto oxidation/reduction of the intermediate reduction product  $UO_2^+$  as shown below also causes redissolution of the cement:



It is, therefore, necessary that in order to prevent the cement passing back into the solution, the velocity of the reduction reaction has to be regulated by carefully controlling the time and pH. A detailed study of the uranium cement formed from pure solutions has to be carried out to understand fully the kinetics of cementation process.



## ACKNOWLEDGEMENTS

We are thankful to Dr. D. N. Wadia, F.R.S., Geological Adviser to the Government of India, for giving an opportunity to present this paper at the symposium and Sri K. K. Dar for the active interest and valuable suggestions given during the course of the work. We are also thankful to Sri M. D. Shirgaonkar and Sri D. Narasimhan, for their suggestions and the analysis of all the samples.

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## DISCUSSION

*Question by Sri D. V. Bhatnagar*

The paper deals with two alternate methods of recovery of uranium from the leach liquors obtained during the heap leaching studies. One is by direct precipitation with sodium hydroxide and the other is by cementation with scrap iron or zinc. Taking into account the composition of the leach liquors and other relevant factors, I feel that the best way of recovering uranium from these solutions will be by employing strongly basic anion exchange resins.

*Answer by Sri K. M. V. Jayaram*

Investigations are at present on hand on the alternative suggested by Sri Bhatnagar. 75 per cent net recoveries are obtained by this method with cake grade of 50.0 per cent  $U_3O_8$ . But keeping in view the difficulties of resin poisoning, etc., and also the inaccessibility of deposits the other two methods are being investigated in detail. This investigation also includes the hydrolysis of  $UO_2$  formed during cementation. If the aim is to produce a crude cake in the field cementation process has definite advantages in certain types of ores like Umra, though copper contamination has to be studied in this case.



## EXTRACTION AND UTILIZATION OF PURE NIOBIUM AND TANTALUM FROM INDIAN ORES

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*(Received 29 April 1969)*

The sister elements niobium and tantalum occur together in nature mainly in the form of the pegmatitic minerals columbite-tantalite, sporadic occurrence of which is known in this country and as pyrochlore.

Niobium metal has been suggested as a possible cladding material for uranium fuels in high temperature fast-reactors. An alloy of zirconium with 2.5 per cent niobium has superior corrosion resistance and strength characteristics commending its application for permanent components in water-cooled nuclear power reactors. In magneto-hydro-dynamics there is a potential demand for niobium-tin and niobium-zirconium super-conducting alloys.

Tantalum finds its main applications in capacitors and tubes in electronic circuits. To a limited extent tantalum is also used in chemical process equipment (on account of its excellent corrosion resistance in chloride media), and as heating elements in high temperature vacuum furnaces.

A new process has been developed for (i) the chemical treatment of Indian columbite-tantalite minerals for the recovery of values and the separation and purification of niobium and tantalum compounds by solvent extraction. (ii) And for the extraction of the pure metals from the intermediates and their further purification and consolidation by electron beam melting and high vacuum sintering. The paper summarizes the progress made to date and the production programme visualized during the IV Plan period.

### INTRODUCTION

The sister elements niobium and tantalum, which belong to Group V-B of the periodic table, are relatively very scarce in the earth's crust, the order of abundance of niobium being around 24 parts per million and of tantalum only 2 parts per million. On account of their very close chemical similarity, the two elements invariably occur together in nature, predominantly in the form of an isomorphous series of oxide minerals, called columbites and tantalites—depending on whether the concentration of niobium or tantalum is greater—



corresponding to the general formula  $[(\text{FeMn})\text{O}(\text{NbTa})_2\text{O}_5]$ . Another important economic source particularly for niobium is the mineral pyrochlore which is essentially a complex niobate of calcium and sodium, containing fluorine ( $\text{NaCaNb}_2\text{O}_6\text{F}$ ).

The major world deposits of columbite-tantalite minerals are located in Nigeria (Africa), and of pyrochlore in Canada, Brazil and Norway, the total reserves amounting to an equivalent of about 1.5 million tonnes of niobium. Production figures reported (Newman 1967) for 1965 are : 2,600 tonnes of columbite from Nigeria, 2,000 tonnes of pyrochlore from Canada and about 1,500 tonnes from Brazil, accounting for about 90 per cent of the total Western world output. The leading consumers of niobium and tantalum mineral concentrates in the world today, for the production of the pure metals and for ferrous and non-ferrous alloys, are the U.S.A., United Kingdom, and West Germany.

In India, sporadic occurrence of columbite-tantalite minerals in pegmatitic deposits has been reported, but production to date has been only very limited. As a definite and growing demand for niobium and tantalum metals and other alloys is foreseen in the alloy steel, nuclear and electronic industries, a more intensive programme of prospecting, mining and processing these minerals is called for.

A survey of the pattern of utilization of niobium in industry indicates that around 85 per cent is consumed in the form of ferro-niobium and ferro-tantalum-niobium in the production of alloy and stainless steels. Niobium, added as ferro-niobium to austenitic chromium-nickel stainless steels, acts as a stabilizer for the carbon by forming the very stable niobium carbide, thus preventing the loss of chromium at the grain boundaries. Type 347 niobium stabilized stainless steel is extensively used in chemical and petroleum processing equipment, operating at high temperatures in corrosive atmospheres, and also in steam turbine generating equipment and high temperature steam lines. From considerations of weld stability, very reliable corrosion resistance and low radiation pick-up, this steel is the popular material of construction for radio-chemical nuclear-fuel processing plants.

Pure niobium metal—which does not have too high a neutron absorption cross-section, has good high temperature strength and is compatible with uranium and liquid sodium—has been used for the canning of metallic uranium fuel elements in fast reactors. A zirconium—2.5 per cent Nb alloy has been suggested for permanent structural components in water-cooled nuclear reactor cores in preference to zircaloy, on the basis of higher strength and greater resistance to hydride attack. There is a potential field of application for niobium-based alloys for high temperature service, as in the aero-space industry, but one of the main problems yet to be solved in this area is protection against atmospheric oxidation. The property of super-conductivity



shown by niobium-tin and niobium-zirconium alloys should create another vital market for the metal in the field of magneto-hydrodynamics, and in the transmission of electric power.

The market for tantalum metal has been steadily growing with its increasing application in the electrical and electronics fields and in materials for the chemical industry. Tantalum in sheet and tube form is used for lining chemical reaction vessels, and in condensers and heat-exchangers. The high reliability, excellent rectification properties, high capacitance and the wide temperature range of application of tantalum capacitors are contributing to a phenomenal growth in demand for them all over the world. In the U.S.A. alone, over 300 million tantalum capacitors, valued at 65 million dollars, were sold during 1965. In India, it has been estimated that the electronic industry in the country would have a requirement of 2.5 million tantalum capacitors/year (estimated at Rs.10 million) by 1975.

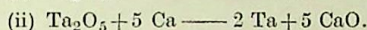
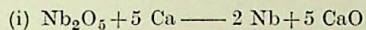
The present paper describes in brief the work carried out in the last few years at the Chemistry and the Metallurgy Divisions of the Bhabha Atomic Research Centre on the processing of Indian columbite and tantalite minerals, and the extraction of pure niobium and tantalum metals, their consolidation and fabrication. Some of the salient features of the chemistry and extractive metallurgy of niobium and tantalum relevant to the discussion that follows are summarized below:

- (a) As stated at the outset, the elements niobium and tantalum, along with vanadium, are members of Group V-B of the periodic table. Niobium resembles tantalum more closely than vanadium. The similarity in chemical behaviour is only slightly less than that between zirconium and hafnium (of Group IV-B), thus posing problems of separation.
- (b) Whereas tantalum predominantly exhibits pentavalency in its compounds, both pentavalent and trivalent niobium compounds are known. The stablest oxides are the pentoxides  $\text{Nb}_2\text{O}_5$  (m.p.  $1512^\circ\text{C}$ ,  $\Delta H_{298} = -455$  k cal) and  $\text{Ta}_2\text{O}_5$  (m.p.  $1877^\circ\text{C}$ ,  $\Delta H_{298} = -488$  k cal) [Wicks and Block]. The oxides are acidic in character and form niobates and tantalates with alkali metal oxides. Sodium niobate and tantalate are sparingly soluble in water, while the potassium compounds are water soluble; they are decomposed on hydrochloric acid treatment to yield the hydrated oxides. The oxides can be brought into aqueous solutions in hydrofluoric acid medium, when anionic species like  $\text{NbF}_7^{--}$ ,  $\text{NbOF}_5^{--}$ , and  $\text{TaF}_7^{--}$  are formed. (Accordingly from low grade columbite tantalite ores, niobium-tantalum concentrates can be made by alkali fusion, followed by hydrochloric acid treatment. Richer minerals can be directly brought into solution in hydrofluoric acid medium.)
- (c) While the classical method of separation of niobium and tantalum is based on fractional crystallization of  $\text{K}_2\text{TaF}_7$  and  $\text{K}_2\text{NbOF}_5$ , the method of liquid-liquid extraction is the one adopted in industrial practice. Solvent extraction of tantalum and niobium from aqueous solution containing hydrofluoric and sulphuric acids is possible either with tributyl phosphate or with methyl-isobutyl ketone. Depending on the acidity and the concentration of the aqueous solution, niobium to tantalum ratio, and organic to aqueous ratio, it is possible to control selective transfer of tantalum and niobium to the organic phase, and selective



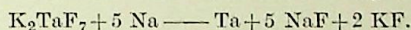
stripping from the organic to the aqueous phase. At the end of the separation and purification operation, tantalum and niobium present in aqueous solution as the anionic fluoro-complex can either be precipitated as the pure hydrated oxides by treatment with ammonia, or isolated as the pure double fluorides ( $K_2TaF_7$  or  $K_2NbOF_5$ ) by addition of potassium fluoride.

- (d) From the pure pentoxides, niobium and tantalum metal powders can be prepared by calciothermic reduction according to the reactions



At the end of the reduction, the metal powders can be isolated by acid treatment of the reduced product to remove calcium oxide. The purity of the powders is determined by the purity of the starting oxide and calcium, and any residual oxygen in the final powder can be removed by high vacuum treatment of pellets prepared from the powder. Alternatively, if extra heat can be supplied in the above reactions by thermal boosters, the reduction can be carried out (with calcium or aluminium) in bomb reactors leading to the formation of consolidated niobium and tantalum biscuits. These biscuits again would require further purification by high vacuum melting prior to fabrication.

- (e) Instead of the oxides, the halides can also be used for the extraction of the metals. Thus  $K_2TaF_7$ , obtained at the end of the solvent extraction purification of the tantalum, can be reduced with sodium according to the reaction



The alkali fluorides associated with the metal can be leached off with dilute acid, leaving pure tantalum powder that has been found to be good enough for capacitor application.

Fused salt electrolysis of the double fluorides and magnesium or sodium reduction of the chloride vapours are some of the other possible routes.

- (f) Both niobium and tantalum are very sensitive to very low levels of oxygen contamination that seriously impairs their ductility. The last traces of oxygen generally found in the as-reduced metals can, however, be removed by high vacuum sintering at temperatures above 2000 °C or by electron beam melting. In either case, the oxygen is removed as the volatile NbO and TaO which have higher vapour pressures than the metals.

### PROCESS DESCRIPTION

The batch of columbite-tantalite ore that has been used in the present investigations contains  $Nb_2O_5$  46 per cent,  $Ta_2O_5$  21 per cent,  $TiO_2$  5 per cent,  $Fe_2O_3$  17 per cent,  $MnO_2$  6 per cent and  $SiO_2$  2 per cent. Starting with this ore, the production of pure niobium and tantalum metal products involves the following major steps:

- (i) Acid treatment of the ore to bring the niobium and tantalum values into solution.
- (ii) Separation of niobium and tantalum by solvent extraction.
- (iii) Preparation of pure niobium and tantalum intermediates.
- (iv) Metallo-thermic reduction of the intermediates to produce the respective metals in powder or consolidated form.
- (v) Cold compaction and high vacuum sintering to produce sintered compacts.



- (vi) Electron beam melting purification of the metals.
- (vii) Fabrication of sheet and wire products.

(i) *Acid Treatment of Columbite-Tantalite*

In view of the high concentration of niobium and tantalum in the ore, direct dissolution of the ore in concentrated hydrofluoric acid has been found to be economically acceptable. From smaller batch studies, it has been observed that optimum dissolution can be obtained in 8–10 hours by using an ore to acid ratio of 1 : 3 (3 kg 40 per cent HF/kg ore) at a temperature of 80–90 °C. In translating these results to handle kilogram batches of the ore, heavy duty polythene tanks have been used to hold the hydrofluoric acid, motor-driven monel stirrers to provide the agitation and steam for heating and maintenance of temperature. The batch dissolution is carried out over a period of 10 hours after which the solution is allowed to settle and is decanted. The feed for the subsequent step of solvent extraction is adjusted by dilution to correspond to a total oxide concentration of about 100 gm/l, and an acidity of 2 N with respect to sulphuric acid and 0.5–1 N with respect to hydrofluoric acid.

(ii) *Separation of Tantalum by Solvent Extraction*

The solvent extraction processes in use abroad for the purification of niobium and tantalum largely employ methyl isobutyl ketone as the solvent. In this system niobium and tantalum are extracted together from the fluoride solution at high acidities, and subsequently selectively stripped from the organic phase. Keeping in view the more urgent demand for tantalum in the country, the possibility of preferential extraction of tantalum at low acidities has been examined here using tributyl phosphate as the solvent. As an organic solvent, tributyl phosphate has advantages over methyl isobutyl ketone on account of its superior chemical stability and low solubility in water.

For the TBP—HF—H<sub>2</sub>SO<sub>4</sub> system the following salient conclusions could be drawn from separatory funnel studies:

(a) A solvent concentration of 50 per cent TBP in kerosene gives optimum extraction characteristics combined with ease of stripping.

(b) With an aqueous phase composition of 100 gm/l (in terms of total oxides)—0.5 N HF—2 N H<sub>2</sub>SO<sub>4</sub> and an organic to aqueous ratio of 1 : 1, 90 per cent extraction of tantalum is achieved with only a minor associated transfer of niobium. In large-scale operation an organic to aqueous ratio of 2 : 1 has been used to effect quicker separation of layers and prevention of emulsification.

(c) A 2-stage scrubbing of the tantalum-laden organic phase with 0.5 N HF—2 N H<sub>2</sub>SO<sub>4</sub>, reduces the niobium contamination in tantalum to less than 250 parts per million. The pure tantalum (in the form of H<sub>2</sub>TaF<sub>7</sub>) can be finally stripped with de-mineralized water.



(d) On completion of extraction of tantalum, the aqueous raffinate can be made up to 5 N HF—9 N  $\text{H}_2\text{SO}_4$  and equilibrated again with fresh TBP to extract the niobium. Niobium is then stripped with de-mineralized water. Based on the above studies, a mixer settler assembly has been designed and fabricated with heavy duty polythene for a tantalum output equivalent to 2 kg of  $\text{K}_2\text{TaF}_7$  per day.

(iii) *Preparation of Pure Niobium and Tantalum Intermediates*

Pure  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$  can be prepared from acidic solutions of  $\text{H}_2\text{TaF}_7$  and  $\text{H}_2\text{NbF}_7$  by ammonia precipitation, filtration, washing, drying and calcination.

1. FLOW SHEET FOR PRODUCTION OF TANTALUM ANODES.

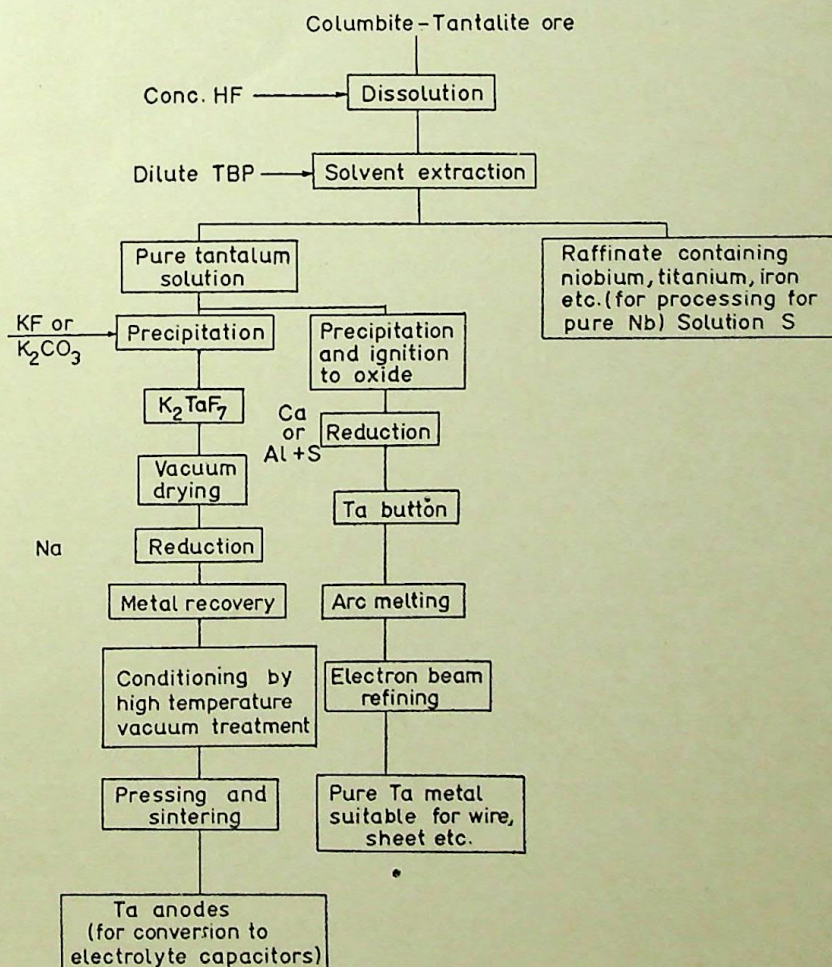


FIG. 1



An intermediate treatment of the hydrated oxide precipitates with concentrated HCl can be incorporated for removal of the last traces of iron and titanium.

For the preparation of  $K_2TaF_7$  (required as an intermediate in the production of capacitor grade tantalum powder) hydrated  $Ta_2O_5$  is dissolved in concentrated HF and the acid solution carefully neutralized with  $K_2CO_3$  to precipitate  $K_2TaF_7$  at a pH around 1-2. The salt is washed with water, and then with trichlorethylene to remove any adsorbed organic matter and vacuum dried to give a white free-flowing powder.

(iv) *Metallothermic Reduction of Niobium and Tantalum Intermediates*

The extractive metallurgy of niobium and tantalum has been reviewed in great detail in the literature (Dowing and Hansen 1963; Gupta and Jena 1965, Kolk *et al.* 1958). The more important methods of obtaining the metals from their intermediate compounds are: (a) reduction of the oxides with metals and non-metals, (b) reduction of halides and double halides with metals and non-metals, (c) fused salt electrolysis of the chlorides and the fluorides, (d) decomposition and disproportionation of the halides.

The method of metallothermic reduction of the oxides and the halides offers various possibilities which have been intensively examined in the Metallurgy Division of the Bhabha Atomic Research Centre. Among the routes examined are calciothermic reduction of the pentoxides to produce the metal powders, sodium reduction of  $K_2TaF_7$  to produce tantalum powder, calcio- and alumino-thermic bomb reduction of the pentoxides to produce the consolidated metals.

The reduction of niobium and tantalum pentoxides with calcium is accompanied by a large release of heat, and if the aim is to produce the metal powders, the reactions have to be tempered by the addition of a heat sink, like calcium chloride. In small-scale studies (Bose *et al.* 1968), it has been observed that an 85-90 per cent yield of niobium and tantalum metal powders can be achieved by using 1.5 moles of calcium chloride per mole of oxide in the charge and 50 per cent of calcium excess. The metal powders are isolated by treating the reduced mass first with cold water and then with dilute hydrochloric acid and aqua regia and finally with distilled water to completely remove calcium oxide and chloride. The powders are washed in acetone and vacuum dried. Under the various conditions studied, it has not been possible to reduce the residual oxygen content in the final metal powders to adequately low levels as specified for capacitor applications. On the other hand, these powders can be purified by electron beam melting and converted to sheet and wire products.

Tantalum metal powder for the production of electrolytic capacitors has to correspond to a very high degree of purity, as laid down in Table I (Belz 1961).



## 2. FLOW SHEET FOR THE PRODUCTION OF NUCLEAR PURE NIOBIUM

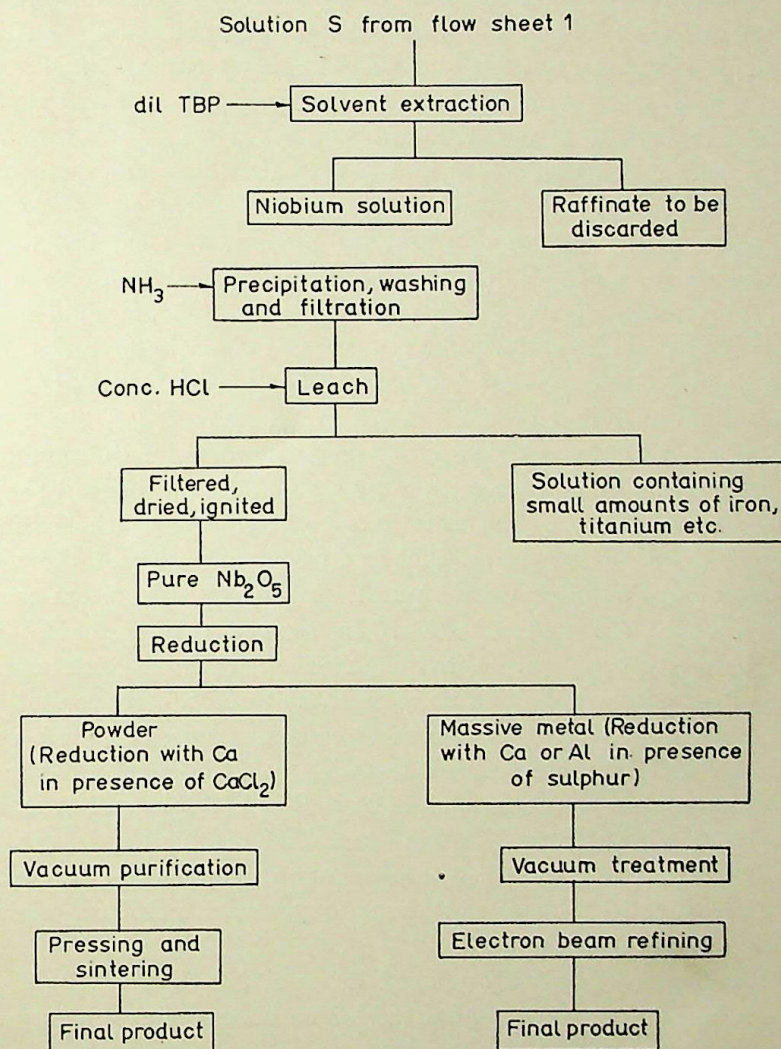


FIG. 2

TABLE I

*Purity specification for capacitor grade tantalum*

Impurities	Nb	Al	Co	Cu	Fe	Mo	Si	Ti	Zr	O	C	N
Maximum tolerance (in parts per million)	140	50	20	50	460	25	780	50	50	930	120	750



Such a purity can be achieved by starting with pure  $K_2TaF_7$  (as available from solvent extraction purification), and carrying out the reduction with high purity sodium. The reduction can be affected in stainless steel batch reactors, using inconel-liners. The  $K_2TaF_7$  charge for the reduction has to be initially vacuum dried, and the charging of the reactor with salt and sodium has to be done in an inert atmosphere to avoid oxygen pick-up during loading and subsequent reduction. The reaction takes place at a temperature around  $900^\circ\text{C}$  after which the charge is cooled, and then treated first with methanol to destroy safely the excess sodium and successively with a series of aqueous reagents to wash off the fluoride slag and the process, as such, has initially been examined on a small scale (Bose *et al.* 1970). An alternate technique would be to react molten  $K_2TaF_7$  with continuous addition of liquid sodium under agitation to promote better contact between the reactants and thereby improve the yield. Conditions for the batch reduction of  $K_2TaF_7$  (2 kg per batch) with sodium have now been optimized at Trombay.

If the aim is not to produce high purity metal powders for the production of sintered components by powder metallurgy techniques, but instead sheet or wire products, consolidation of the metal can be attempted at the reduction stage itself. However, as it will be difficult to control purity of the metals at the reduction stage an intermediate purification by electron beam melting would be necessary prior to fabrication. In such a scheme, oxide intermediate can be used which will be less expensive than halide intermediate. The number of steps involved could be reduced and accordingly capital costs may also be expected to be less. From these considerations, the bomb reduction of niobium and tantalum pentoxides with calcium and also the less expensive aluminium has been examined in great detail [Gupta and Jena 1964, 1965, 1968, 1969]. As both niobium and tantalum are high melting metals (m.p. : Nb— $2468^\circ\text{C}$ , Ta— $2996^\circ\text{C}$ ), it is necessary to supplement the heat of reaction in these cases with booster reactions to promote metal consolidation and better slag-metal separation.

In bomb reduction tests, with pound batches of  $Nb_2O_5$  with 40 per cent excess calcium and 20 per cent sulphur (added as booster) in refractory-lined steel bombs pre-heated to  $500^\circ\text{C}$  consolidated niobium metal yields of 82–84 per cent have been achieved. In similar tests carried out with  $Ta_2O_5$ , the consolidated metal yields have been of the order of 70 per cent. Analysis of the as-reduced metals and purification achievable by electron beam melting are shown in Table II.

In place of calcium which is expensive and has to be imported, aluminium can also be used for the bomb reduction of  $Nb_2O_5$  or  $Ta_2O_5$ . Though the heat available from aluminothermic reduction is considerably less than that in calciothermic reduction, the lower melting point of  $Al_2O_3$  ( $2030^\circ\text{C}$ ) is an advantage. The melting point of the slag can be further lowered by so



TABLE II  
*Analysis of ca-reduced and electron beam melted samples of niobium and tantalum*  
 Analysis (in parts per million)

	Ta	Nb	B	Al	Pb	Cu	Co	Sn	Ca	S	Fe	Sb	Cr	Mg	Si	O	C	N
Ca-reduced niobium button ..	500	-	0.5	150	10	250	5	8	7000	810	1000	8	250	250	250	650	850	150
Electron beam melted niobium ..	500	-	0.5	100	10	10	5	8	400	210	75	8	20	150	150	150	90	58
Ca-reduced tantalum button ..	-	600	-	10	25	10	10	10	2400	600	500	25	-	200	600	1080	600	110
Electron beam melted tantalum ..	-	500	-	10	10	10	10	10	350	10	10	25	-	10	100	150	96	80



composing the charge that an  $\text{Al}_2\text{O}_3$ — $\text{Al}_2\text{S}_3$  eutectic (m.p. 1100 °C) is formed in the reduction. Making use of this principle, alumino-thermic reductions have been successfully carried out to achieve an 88 per cent yield of niobium and tantalum metals. The composition of the as-reduced metals and their further purification by electron beam melting is shown in Table III.

TABLE III  
*Analysis of the principal constituents of alumino-thermically reduced and electron beam refined samples of niobium and tantalum*

Description of the metal		Elements (per cent)				Hardness (DPh)	Workability
		Al	C	N	O		
Al-reduced button	niobium	2.82	0.023	0.04	0.81	380	No reduction sustained by the metal sample
Electron beam melted	niobium	< 0.005	0.012	0.005	< 0.02	90–100	Easily fabricated to strips and wires
Al-reduced button	tantalum	1.08	0.025	0.035	0.74	N.D*	No reduction sustained by the metal sample
Electron beam melted	tantalum	< 0.005	0.0155	0.0035	0.014	80	Cold rolled giving more than 95% reduction without intermediate annealing

\* N.D.—Not determined.

### *Consolidation and Purification of Niobium and Tantalum*

The production of fabricated shapes of niobium and tantalum involves either (i) high vacuum powder metallurgy techniques, or (ii) electron beam melting of ingots which can then be processed for rolling of sheet, extrusion of tubes, or wire drawing.

The tantalum electrolytic capacitors that are now in great demand in the country have to be produced from high purity tantalum powder (as available from sodium reduction of  $\text{K}_2\text{TaF}_7$ ) by cold compaction, followed by high temperature high vacuum sintering. The specifications for the tantalum capacitors lay down a high standard of purity, a close control of size distribution in the starting powder, and close control of size and porosity distribution in the sintered anodes to ensure a very low leakage current, a very low dissipation factor, and a high capacitance. From a detailed study of powder



characteristics, compacting and sintering conditions, production of tantalum anodes, meeting stringent specifications has been optimized at Trombay. While the production of the green tantalum compacts is done with specially designed dies in hydraulic pressing devices, the final sintering under controlled conditions is carried out under a very high vacuum, in a tantalum resistance furnace at temperatures around 2000 °C. The further production of tantalum capacitors from sintered tantalum anode slugs involves (a) anodizing of the slug to form a thin polarizable layer of  $Ta_2O_5$ , (b) vacuum impregnation with manganese nitrate which is then decomposed to form  $MnO_2$ , (c) coating with graphite, and (d) encapsulation.

The technique of electron beam melting has come to commercial prominence mainly in the context of niobium and tantalum metallurgy. The electron beam furnace makes use of a stream of electrons (generated from a heated tungsten filament), accelerated with the help of electro-magnetic lenses to impinge on the feed material and dissipate their kinetic energy as heat. With this technique, a molten pool of metal can be maintained at will under adequate super-heat and high vacuum to enable the removal of metallic and interstitial impurities from niobium and tantalum. The Technical Physics Division of the Bhabha Atomic Research Centre has designed and commissioned electron beam button and ingot melting furnaces which have been used for the purification of niobium and tantalum.

### CONCLUSION

From the columbite-tantalite ore to the finished niobium and tantalum product is a long flow-sheet and a complex technology, involving toxic and corrosive reagents, reactive metals requiring special handling, and sophisticated high vacuum techniques, all of which account for the high costs of the end products. Based on the know-how developed at Trombay, plans have been finalized for the setting up of a tantalum capacitor industry at Hyderabad. The niobium by-product that will become available in this operation can be processed to produce either pure niobium alloys depending on the demand. The Electronics Committee Report of the Government of India has estimated the demand for the tantalum capacitors at 5 tonnes tantalum metal per year by 1975.

### ACKNOWLEDGEMENTS

The authors gratefully acknowledge the continued help and encouragement of Dr. J. Shankar and Dr. G. S. Rao, Chemistry Division, and of Shri C. V. Sundaram, Metallurgy Division, in the development programme of niobium and tantalum at the Bhabha Atomic Research Centre.



## DISCUSSION

*Questioner's name:* D. V. Bhatnagar

*Question:*

Quite frequently uranium is associated with niobium and tantalum ores. During the proposed attack on the mineral by hydrofluoric acid the uranium in the lower valency state will be precipitated and that in the higher state will go into solution. Has provision been made for the recovery of uranium in the proposed flow-sheet?

*Answer by* Dr. J. Shankar

Yes, uranium has been found in such minerals and provision has been made to recover uranium, if present in the ore.

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SOME OBSERVATIONS ON URANIUM-COPPER RELATIONSHIP IN  
THE SURDA COPPER MINES AND THEIR BEARING ON THE  
ZONING OF MINERALIZATION IN THE SINGHBHUM  
THRUST BELT, BIHAR

by K. K. SHARMA, *Department of Atomic Energy,  
Atomic Minerals Division, New Delhi 22*

(Received 29 April 1969)

The uranium and copper lodes in the 5th level of the Surda Mines show similar spatial disposition and reveal a sympathetic distribution in a selected part. Data from Roam-Rakha and Mosaboni-Badia sections show a gradual separation of uranium and copper, while Keruadungri-Jaduguda and Kanyaluka-Bhalki sections mark a clear separation of the two.

The present studies suggest three horizontal zones in the Singhbhum Thrust Belt—a central zone and an intermediate zone which include all the important deposits of copper and an outer zone showing all the uranium deposits known so far.

It is further suggested here that the focus of mineralization was close to Surda-Pathargarah area and that migration of fluids laterally on both sides developed a gradual separation of uranium and copper, resulting in the above-mentioned zones of mineralization. No major time gap between the uranium and copper mineralization is conceived.

INTRODUCTION

Detailed geological investigations along the Singhbhum Thrust Belt since 1950 have indicated certain distinct uranium-copper field relationships and these have been dealt with, in detail, by Bhola (1964) and Bhatnagar *et al.* (1964). The hypogene ore mineralization in this area is described to have taken place in three major phases separated by a time gap—an early oxide phase (apatite-magnetite) followed by a phase of uranium mineralization and an end phase of sulphide mineralization (Bhola, *op. cit.*; Sarkar 1966a). The coincidence of uranium and copper lodes in Tamapahar, Rakha Mines and Roam-Sidheswar areas has been explained as due to the reopening of the already mineralized fractures and subsequent deposition of lower temperature ore (sulphide) minerals (Bhola, *op. cit.*).

In the present work studies have been concentrated on the behaviour of uranium lodes in the 5th level of the Surda Mines (I.C.C.) and its relationship with copper mineralization in space and time. An attempt has been made to divide a part of the thrust belt into three zones on the basis of uranium-copper relationship. Some data have also been collected from



various bore holes drilled in Roam-Rakha and Mosaboni-Badia sections and from the underground groove sampling in the Badia Mines for uranium.

#### GEOLOGICAL SETTING

The Surda Copper Mines ( $22^{\circ} 33' 45'' : 86^{\circ} 26' 15''$ ) of Indian Copper Corporation (P.) Ltd. is located in the Singhbhum District of Bihar and is nearly 5 km N.  $30^{\circ}$  W. of the well-known Mosaboni Copper Mines ( $22^{\circ} 31' : 86^{\circ} 28'$ ). A very good review of the geology of this part of the belt has been given by Sarkar (1966b). The rock types consist of garnetiferous mica schists, quartzites, quartz-kyanite-schist, quartz-chlorite-biotite-schist, basic schists and epidiorites, belonging to the Chaibasa Stage and the Dhanjori Group of Dunn and Dey (1942).

In the Surda Mines there are three copper lodes, the Footwall Lode, the Hangwall (Hanging-wall) Lode and the North Surda Lode, besides thin sulphide stringers and disseminations here and there. These lodes are arranged in *en échelon* pattern. The quartz-chlorite-biotite schist with intervening lenticular bands of quartzites, lenses of basic schists and vein quartz is the main host rock for the sulphide lodes.

#### PRESENT OBSERVATIONS ON THE URANIUM-COPPER MINERALIZATION IN THE SURDA MINES

On the basis of the results obtained by the radiometric checking of the rock dumps near the Tamajuri shaft, systematic groove sampling was undertaken in the 5th level (Maximum developed) of the Surda Mines. Samples taken from the cross-cuts did not provide encouraging results except those taken from near the Hangwall drive which exposes the copper lode. The average equivalent  $U_3O_8$  content of the samples taken from the cross-cuts is of the order of about 0.004 per cent and rarely 0.01 per cent, while the samples collected close to the copper lode (near the Survey Station 7X) and also along the copper lodes have shown significantly higher concentration of uranium (0.02 to 0.053 per cent  $eU_3O_8$ ).

#### *Geological Data from the Surda Mines*

The mapping of the Hangwall Copper Lode and the North Surda Lode on a scale 1:200 and plotting of the equivalent uranium values obtained from the groove samples have shown that the uranium lodes coincide quite closely with those of copper. Though the lodes of both uranium and copper appear to be simple at some places, they become complex and get mixed up with 'veinstone' elsewhere. They have the tendency to swell and pinch; send off offshoots both towards hanging-wall as well as foot-wall side; divide into branches which after taking independent courses from 3 to 30 m again



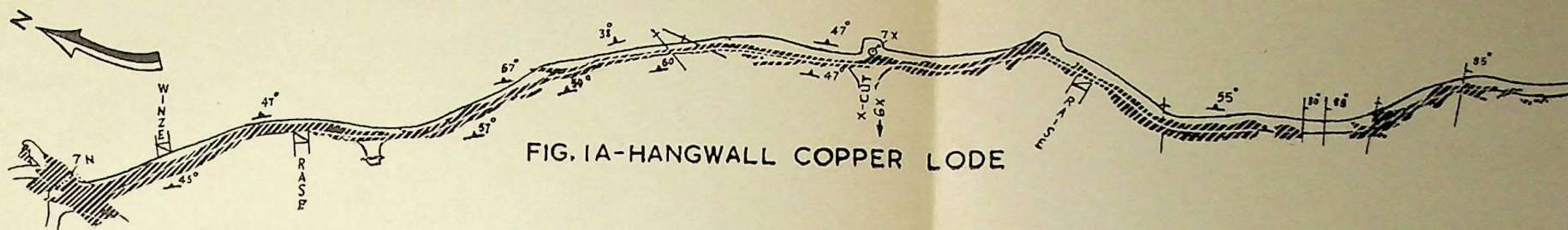


FIG. 1A-HANGWALL COPPER LODE

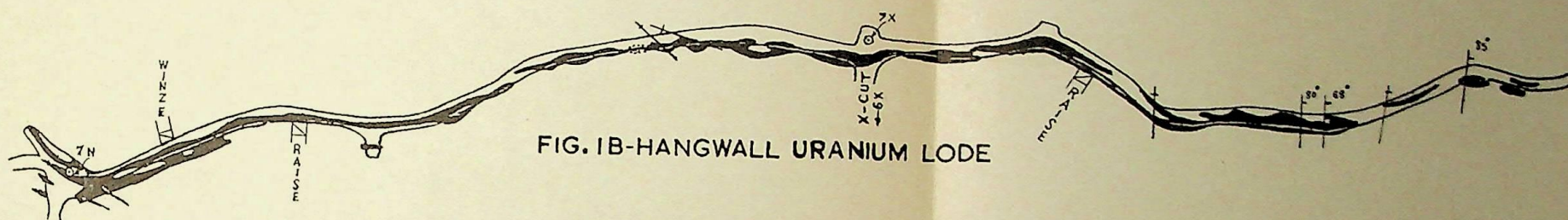


FIG. 1B-HANGWALL URANIUM LODE

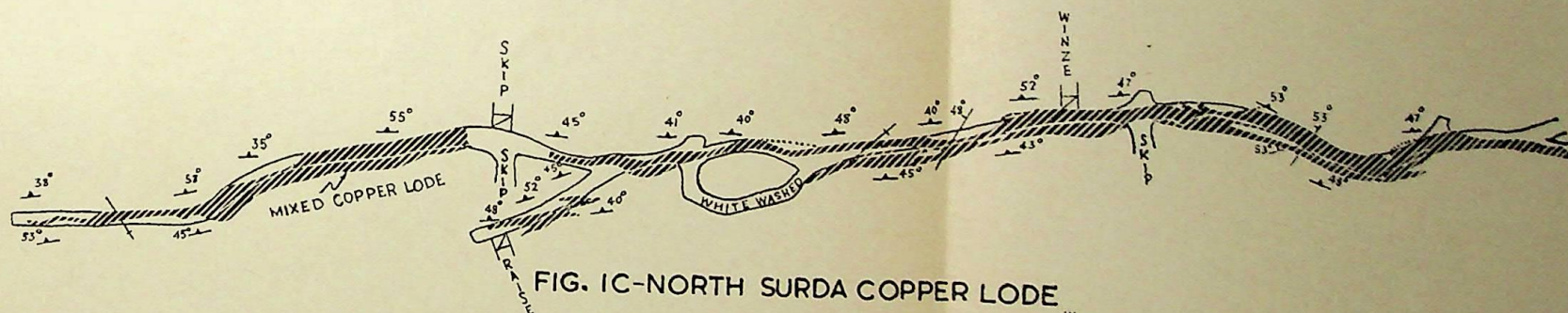


FIG. 1C-NORTH SURDA COPPER LODE

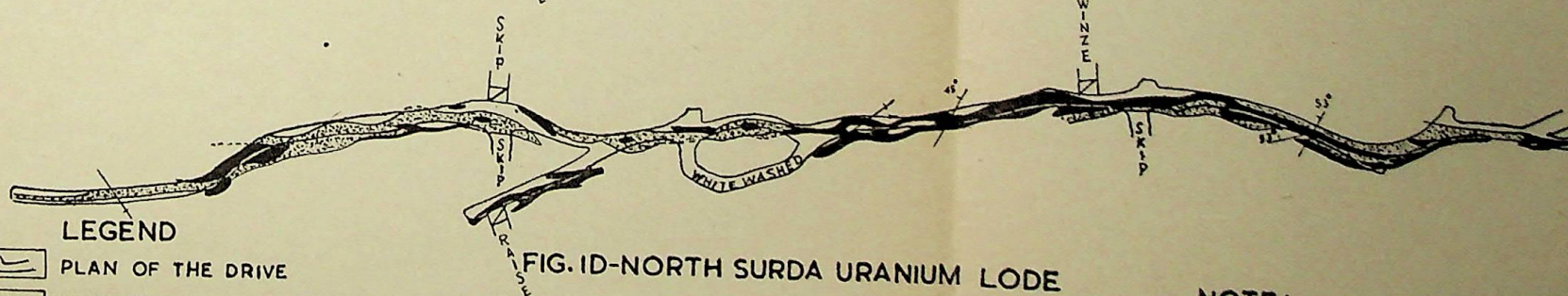


FIG. 1D-NORTH SURDA URANIUM LODE



SCALE, 1:1000  
M 10 5 0 10 20 30 M

**NOTE:**

1. Plane of Projection is "back".
2. Foliation dip has been taken as 45° for purpose of Projection of geological and radiometric data.







converge and rejoin the parent lode, enclosing thereby 'horses' and quartz 'veinstone'.

The following evidences indicating some kind of structural control responsible for the similarity in spatial disposition of uranium and copper mineralization in the Surda Mines (Fig. 1) are significant:

1. The shattering effect by the post-mineralization fractures and minor faults, in both the Hangwall uranium lode as well as the copper lode towards their southern end, is similar.
2. The presence of two similarly placed veins of uranium and copper with a correlatable barren zone between the two, observed at 55 m south of the Survey Station 7N.
3. The close similarity in gradual swelling from south to north and later waning with offshoots, of the lode of uranium and copper near the Survey Station 7N.
4. The similarity of the courses adopted by the North Surda lodes of uranium and copper after branching at 70 m south of the skip connecting the 4th and 6th levels.
5. The western branch of the lode of uranium and copper exposed in the small dead end of the North Surda Drive show similarity in their spatial disposition.

The spatial parallelism shown by the lodes of uranium and copper in this area has most probably taken place due to mineralizing solutions pervading all fractures and other structurally favourable places, rather than by reopening of earlier mineralized fractures to be filled again by later sulphide minerals (Bhola 1964). In fact, in the absence of any secondary fractures filled by the later sulphide minerals free of uranium, nor cross-cutting of uranium veins by subsequent sulphide phase is evidence dis-favouring the latter view.

#### *Chemical and Radiometric Data from the Surda Mines*

Thirty chemical analyses for copper and the corresponding equivalent uranium values ( $eU_3O_8$  per cent) are provided in Table I. The relationship of Cu *v.*  $eU_3O_8$  in the Surda area is diagrammatically shown in Figs. 2b and 3 and for comparison the similar data from adjoining areas of Rakha and Mosabani Mines are shown in Fig. 2a and 2c (data collected from Shirke and Sharma (1966), Sharma (1967) and Gangadharam *et al.* (1963)). The linear Cu- $eU_3O_8$  relationship in the Surda area is clearly brought out in Fig. 2b and this is in sharp contrast with that of adjoining Rakha and Mosabani areas. This behaviour is attributable to changing composition of mineralizing solution. It may be of interest to note in this connection that a grab sample collected from the rock dump of the Pathargarah Mine (believed to be the



south-eastern continuation of the Surda mineralization) analysis 0.13 per cent  $eU_3O_8$  forms a copper rich fraction whereas the copper impoverished fraction analysed only 0.034 per cent  $eU_3O_8$ .

The data being obtained from the groove samples taken from the 4th and 6th levels of the Surda Mines also confirm the relationship established in the 5th level (i.e. coincidence of uranium and copper lodes). Further work in the Surda Mines is in progress.

TABLE I  
*Average equivalent uranium and copper contents of  
the 30 groove samples*

Sl. No.	Distance from the Survey Station 7X (in metres)	Average copper content (per cent)	Average equivalent uranium content (per cent)
(a)	(b)	(c)	(d)
1	4.6	3.56	0.026
2	7.2	2.67	0.023
3	8.6	2.37	0.020
4	11.8	2.59	0.023
5	16.4	3.45	0.032
6	19.0	2.60	0.029
7	20.6	2.25	0.026
8	24.6	4.15	0.032
9	28.6	2.11	0.022
10	36.0	3.84	0.028
11	37.4	3.59	0.027
12	46.2	2.00	0.020
13	56.6	2.39	0.021
14	59.8	1.57	0.020
15	76.5	2.80	0.022
16	81.4	2.57	0.022
17	94.5	2.45	0.033
18	99.3	2.56	0.022
19	100.8	3.02	0.029
20	102.0	3.33	0.035
21	109.5	3.20	0.030
22	111.0	2.65	0.024
23	114.0	1.74	0.021
24	115.0	2.26	0.023
25	118.0	2.72	0.023
26	123.5	3.19	0.029
27	125.0	2.31	0.030
28	126.4	2.64	0.029
29	127.9	2.52	0.027
30	129.2	2.65	0.031



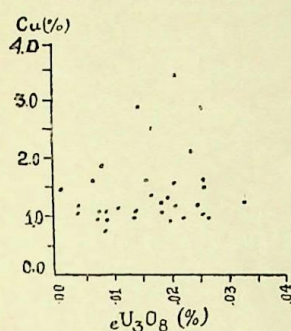


FIG2a-GRAPH SHOWING  
URANIUM-COPPER  
RELATIONSHIP  
IN THE  
RAKHA MINES

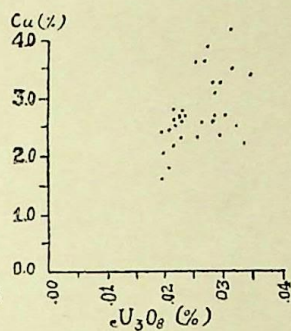


FIG2b-GRAPH SHOWING  
URANIUM-COPPER  
RELATIONSHIP  
IN THE  
SURDA MINES

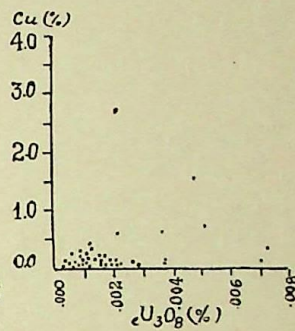


FIG2c-GRAPH SHOWING  
URANIUM-COPPER  
RELATIONSHIP  
IN THE  
MOSABONI MINES

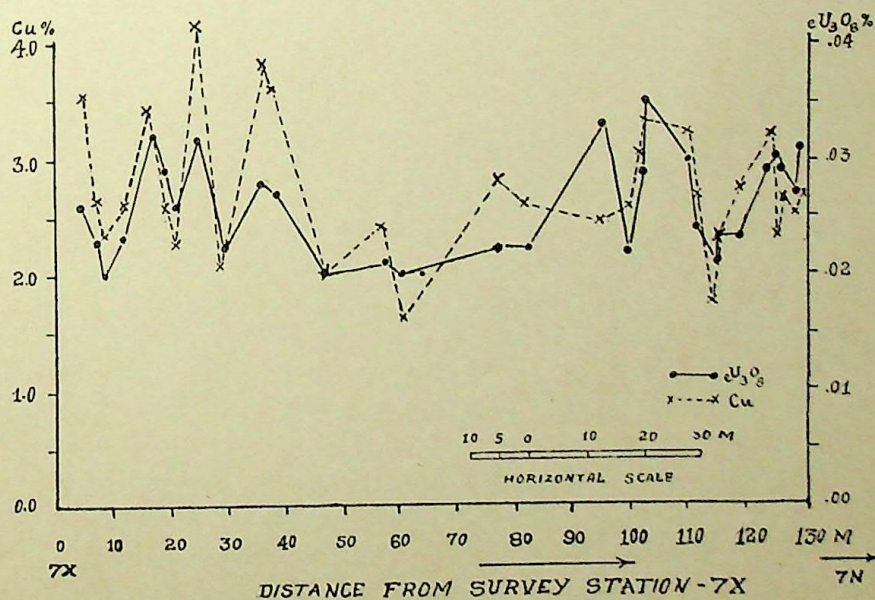


FIG.3 - DISTRIBUTION DIAGRAM OF  $U_3O_8$  AND Cu, SURDA MINES

FIGS. 2 and 3



# SOME DATA ON URANIUM-COPPER RELATIONSHIP IN TAMAPAHAR, RAKHA MINES AND ROAM-SIDHESWAR AREAS

The core sample assay results in respect of copper and uranium contents and gamma-ray logging data, collected by Shirke and Sharma (1966) and Sharma (1967), of 150 bore holes so far drilled by the Geological Survey of India (Exploratory Wing) in Tamapahar, Rakha Mines and Roam-Sidheswar blocks bring out the following relationship between uranium and copper mineralization:

- (a) The lodes of copper and uranium, in general, coincide in the Roam-Sidheswar Block except in bore hole Nos. RMS-21, 43 and 49 and RMS-22, where an independent uranium lens has also been noted towards hanging-wall and foot-wall side of the copper-uranium lodes respectively.
- (b) Besides the combined uranium and copper lodes, independent uranium lenses have been noted in good number in the Rakha Mines Block

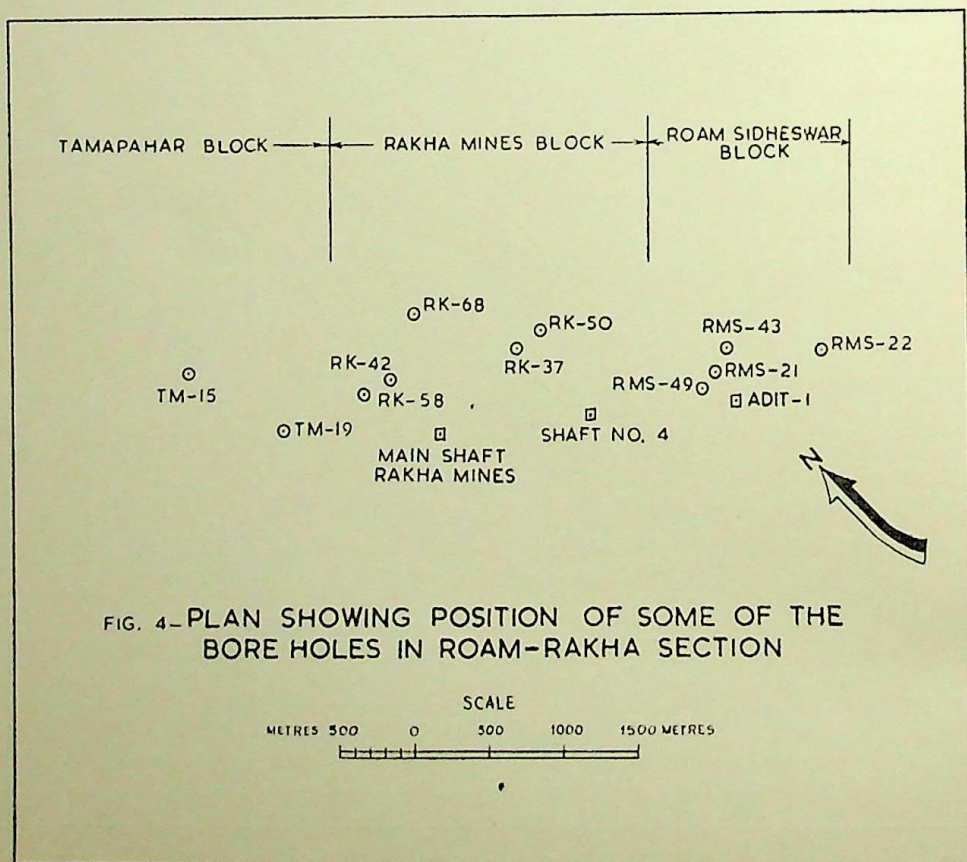


FIG. 4-PLAN SHOWING POSITION OF SOME OF THE BORE HOLES IN ROAM-RAKHA SECTION

Fig. 4



and they increase towards the western end. Three hanging-wall and two foot-wall lenses in bore hole RK-42 and four hanging-wall lenses in bore hole RK-68 have been noticed while RK-37, 50 and 58 recorded only one uranium lens (Fig. 4).

- (c) Similarly, also in the Tamapahar Block independent uranium lenses have been noted which show an increase in number towards the western side of the block (five hanging-wall and one foot-wall lens in TM-15 and three hanging-wall lenses in TM-19).

The foregoing observations indicate the development of increasing number of independent uranium lenses from east (Roam-Sidheswar Block) to west (Tamapahar Block), thus suggesting a progressive trend in the separation of uranium.

Also an erratic behaviour of uranium and copper distribution, based on the core samples assay results for equivalent uranium and copper contents, in these blocks has been noted (Fig. 2a).

#### URANIUM-COPPER RELATIONSHIP IN THE BADIA MINES

Geological mapping and the groove sampling undertaken in the 6th, 7th, 8th, 9th and 10th levels of the Badia Mines (I.C.C.) during the year 1955 by the Atomic Minerals Division indicated that the uranium though closely associated with copper is not persistent all through. Small lenses of uranium, of an average grade 0.024 to 0.034 per cent  $eU_3O_8$ , are found enclosed within the copper lode (Krithiventy 1955).

The gamma-ray logging of I.C.C. bore holes (Nos. 209, 210 and 215) drilled in the Badia Mines block has indicated a few independent uranium lenses, mostly towards the hanging-wall side of copper-uranium lodes.

#### ZONING IN THE SINGHBHUM THRUST BELT

The data described in earlier pages adequately bring out certain definite zones in the uranium-copper relationship. It is proposed here that the thrust belt be divided into three zones based on their interrelationships (Fig. 5):

- (a) *Central Zone*, comprising of Surda-Pathargarah area, where the lodes of uranium and copper coincide and a sympathetic distribution of the two is discernible.
- (b) *Intermediate Zone* includes the Mosaboni and Badia Mines on the south-eastern side and Tamapahar, Rakha Mines and Roam-Sidheswar areas on the north-western side of the central zone. Here, while uranium mineralization generally coincides with copper, no systematic relationship in the distribution of uranium and copper has been noted. This zone is also characterized by the gradual separation of uranium from copper-uranium mineralizing solution and the development of independent uranium lenses.



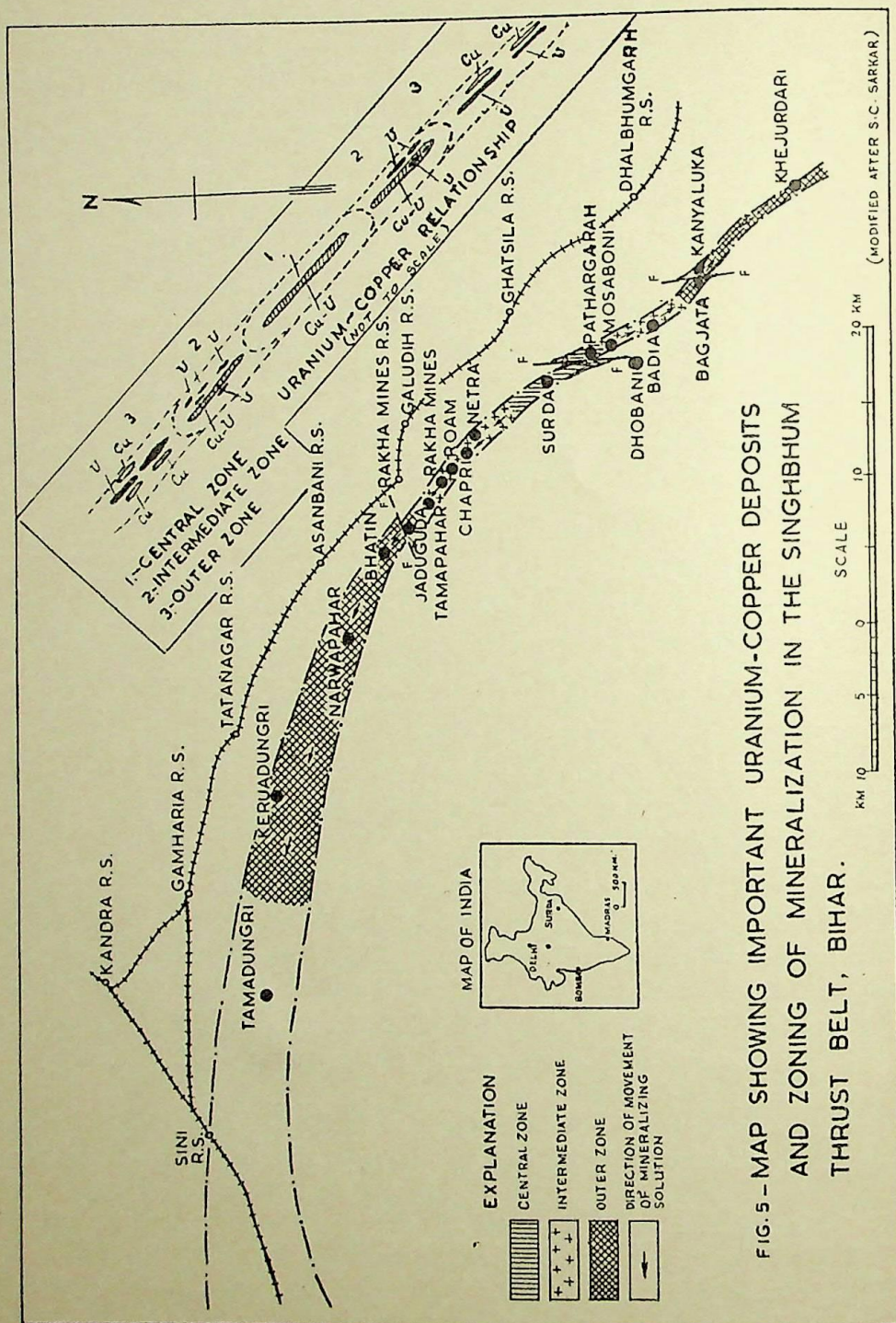


FIG. 5



- (c) *Outer Zone* flanks intermediate zone on the two sides and includes Jaduguda, Bhatin, Narwapahar, Keruadungri and beyond towards north-west and Kanyaluka-Bhalki towards south-east. In this zone, the lodes of uranium and copper are well separated and distinct from each other (cf. Bhola, op. cit.). The sulphide lodes occur either to the hanging-wall or to the foot-wall side of the uranium lode. At places, thin zones of copper are found to have cut across the uranium lodes.

In the Singhbhum Thrust Belt all the important deposits of copper with some uranium are located in the central and the intermediate zones, while the outer zone includes all the uranium deposits so far known.

The zoning of uranium-copper mineralization in the Singhbhum Thrust Belt appears mostly horizontal, although some vertical zoning may also be present. An attempt has been made here to explain this zoning by the lateral movement of the mineralizing solution along the shear zone both towards north-west and south-east of the probable source.

The mineralizing solutions giving rise to the deposits of uranium and copper in this region appear to have operated from a focus close to the Surda-Pathargarah area (the central zone). These solutions after having moved upwards into the shear zone, moved laterally both towards north-west and south-east under the effect of the mass movement of the hydrothermal solution itself (Howkes and Webb 1962). This mineralizing solution, more enriched in uranium in its early stage, due to falling temperature, difference in mobility and movement along the shear zone for a considerable distance, resulted in the gradual change in its composition and finally in the separation of uranium and copper, yielding separate lodes of the two in the outer zone. All the well-known deposits of uranium in the Singhbhum Thrust Belt such as Narwapahar, Bhatin, Jaduguda and Kanyaluka and also presently coming-up deposit at Bagjata are located in this outer zone.

The formation of the intermediate zone is attributed to the mineralizing solution, having undergone some impoverishment in uranium and a rise in the concentration of copper at the source, which due to comparatively more restricted movement resulted in the development of only a localized variation in the composition represented by small lenses of uranium enclosed in the copper lode and irregular distribution of uranium and copper. The frequent development of independent uranium lenses towards the hanging-wall and the foot-wall sides of the copper-uranium lodes near the outer margins of this zone indicates some separation of uranium from the copper-uranium solution which formed the copper-uranium lodes.

The last stage of the activity of the mineralizing solution is marked by the formation of the central zone, where the two constituents were deposited



together in marked parallelism with each other as a result of slow cooling and localization by stagnation.

#### CONCLUSION

The foregoing discussions about the Surda-Pathargarah and other adjoining regions of the Singhbhum Thrust Belt lead to the tentative conclusion that the mineralization of the two metals, viz. uranium and copper, are not separated by any major time gap, the two having resulted from a single continuous process of deposition from a mineralizing solution containing both the metals.

This solution having moved upwards into the shear zone from a focus close to the Surda-Pathargarah area spreads laterally towards the north-west as well as the south-east along the shear zone and has given rise to three distinct zones.

The presence of uranium and copper lodes together in this part of the Singhbhum Thrust Belt is due to precipitation of the two from the same solution followed by deposition in the structurally favourable places in the shear zone and not due to deposition of copper in reopened fractures already mineralized with uranium.

#### ACKNOWLEDGEMENTS

I am grateful to Dr. D. N. Wadia, F.R.S., National Professor and Geological Adviser to the Government of India, for permitting me to present this paper. My thanks are due to Mr. K. L. Bhola for constant encouragement in the preparation of the paper and to Dr. T. K. Bhattacharyya and Mr. B. D. Chatterjee for critical discussions and valuable suggestions. Thanks are also due to Mr. Y. N. Rama Rao for his valuable guidance in the field. The help rendered by Messrs Indian Copper Corporation (P.) Ltd., by way of permitting me to work in their mines and by making available their mine plans and assay values, is also acknowledged.

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### DISCUSSION

*Questioner's name:* Dr. K. K. Majumdar

*Question:*

I would like to draw the attention of the author whether he has noticed any relationship between uranium and copper minerals and chlorite in the Singhbhum Thrust Belt. We have observed that as we move West or North-westwards from Mosabani area, we find that copper mineral decreases and chlorite and uranium minerals rise.

*Author's reply:*

Wall rock alteration studies by many workers have indicated that biotitization and chloritization of the rocks are as a result of intense hydrothermal activities in the Singhbhum Thrust Belt. Biotitization is more characteristic of apatite-magnetite mineralization, while chloritization is more with uranium and sulphide mineralization. Some of the chlorite developed towards north-western part of the belt may also be as a result of the second metamorphism which does not rise above lower green schist facies.

20/11 (K. K. Sharma)

*Questioner's name:* Dr. G. R. Udas

*Question:*

The polished sections of U ore are corroded by chalcopyrite indicating U ore mineralization earlier than copper. The conclusions therefore need be guarded.

*Author's reply:*

Like uraninite, pyrite and pyrrhotite are also corroded and replaced by chalcopyrite which is itself being marginally replaced by chalcocite and covellite. So the polish section studies indicate only the relative position of uraninite and sulphide minerals and not the time gap between the two.

15/11 (K. K. Sharma)

*Questioner's name:* Dr. A. G. Jhingran

*Question:*

The data from Roam-Sidheswar showed that bulk of mineralization is only of copper and only 2 or 3 holes gave uranium value. Hence his observation that uranium and copper mineralization which coincides in this belt need to be checked.



I also think that uranium and copper mineralization has taken place by far and large in separation phase.

*Author's reply:*

The assay results in respect of copper and uranium from the available core samples of the bore holes drilled in the Roam-Sidheswar Block have shown that uranium is associated with copper in all cases. The observation that uranium and copper mineralization coincides in this part of the belt is a well-established fact recognized by all.

Regarding separate phases of uranium and copper mineralization it may be pointed out here that the field evidences on the bases of which Dunn (1937) brought in the concept of two-phase—oxide phase and sulphide phase—mineralization in the Singhbhum Thrust Belt are not seen in the Surda Mines where detail underground mapping in the 5th level was done by the author. The similar spatial disposition and the same degree of shattering suffered by the lodes of uranium and copper in the Surda Mines are the evidences contrary to those used by Dunn.

15/11 (K. K. Sharma)



## CARBONATITES OF SEVATHUR AND JOKIPATTI, MADRAS STATE, INDIA

by G. R. UDAS\* and P. KRISHNAMURTHY, *Centre of Advanced Study in Geology, University of Saugar, Saugar, M.P. (India)*

(Received 29 April 1969)

The paper describes the geologic setting, mineralogy and geochemistry of the economic minerals of the carbonatites of Sevathur and Jokipatti, Madras State. The carbonatites were apparently emplaced  $720 \pm 30$  million years ago along the boundary fault zone between orogenic belts and are associated with syenites. Pyroxenites and fenites occur within the oval-shaped aureole of fenitization surrounding the carbonatite body. The carbonatites are composed of sövites in the outer periphery and beforsite in the inner core, with ankeritic carbonatite forming a thin transitional zone between the two. The carbonatites are characterized by fairly high radioactivity (0.01–0.04 per cent  $eU_3O_8$ ), enrichment in  $ThO_2$ , Sr, La, Ce, Nb and Ba and the expected magnitude of  $Sr^{87}/Sr^{86}$  ( $0.705 \pm 0.0007$ ). The high phosphorous content of the rocks (1.21–14.22 per cent  $P_2O_5$ ) and the soils (4–11 per cent  $P_2O_5$ ) makes the area an attractive source of raw materials for the fertilizer industry. Possible structure and age clues for locating carbonatites in the southern peninsula of India are indicated.

### INTRODUCTION

The two occurrences of carbonatite alkaline complexes at Sevathur and Jokipatti, located at a distance of about 20 kilometres from each other, promise a good prospect for economic exploitation chiefly of phosphates and niobium, rare earth-bearing radioactive minerals and vermiculite. The carbonatite bodies are intrusive into the gneisses. Their brecciated contact with the country rock, the arcuate, concentric carbonatite dykes around the main mass as also the radial dykes observed in the well cuttings surrounding the carbonatite establish beyond doubt the intrusive nature of the carbonate rock. Typical mineral assemblage of calcite, dolomite, magnetite, apatite, monazite, pyrochlore, calzirtite, yttrözircon, with sodic pyroxenes; sodic amphiboles crossite and richterite, arfvedsonite; sphene, perovskite, vermiculite, nepheline and pyrite in carbonatites and fenites enlist these complexes in the group of apatite-magnetite type of Pecora (1956). The metasomatic aureole around the carbonatite body giving varied fenites, pyroxenites, and the ijolitic group of rocks are described. The metasomatic aureoles within the Dharwar gneissic complex are caused by carbonatite, and compare favourably with those referred to by Mekie (1966). The  $Sr^{87}/Sr^{86}$  ratio of  $0.705 \pm 0.0007$  and K/Ar determination of  $720 \pm 30$  m.y. were kindly provided by Dr. T. Deans of

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the Institute of Geological Sciences, U.K. The syenite ring complex at Elagiri and the intrusive syenites exposed to the south of the Sevathur complex and north of the Jokipatti complex link the genetic relationship of the carbonatite with the alkalie rocks.

#### PREVIOUS WORK

The geological literature of the old North Arcot district refers to an east-northeasterly faulted contact between the gneisses and charnockites in the area. 'The bed of river Palar' just two miles north of Jolarpet (Latitude  $12^{\circ} 30'$ : Longitude  $78^{\circ} 30'$ ) which flows through the northern part of the Sheet No. 57 L/13 'appears to be a line of fault. There are several parallel zones showing crushing' (Pascoe 1926). He further quotes (Fermor 1936) that 'the rocks south of Palar are charnockites whereas to the north acid granites are found'. This is the only significant mention from the old records of the Geological Survey of India.

While prospecting for vermiculite at Sevathur Shri V. Gopal of the Madras State Geology Department collected samples from this area. These were seen by Dr. D. N. Holt, the U.N. Hydrological expert of the tube-well organization, and were suspected by him to be carbonatites. T. Deans after his laboratory work and a short field trip confirmed the occurrence at Sevathur to be a carbonatite (Deans 1967). The authors undertook detailed investigation, and during their survey discovered another occurrence of carbonatite alkalie complex at Jokipatti.

#### LOCATION

Sevathur (Lat.  $12^{\circ} 25'$ : Long.  $78^{\circ} 32'$ ) can be approached from Tirupattur by a rail link along Jolarpet-Salem line of the Southern Railway. Carbonatite outcrops are located about half a mile east of Sevathur village. The carbonatite outcrops at Jokipatti are located a quarter of a mile east of the village. It can be approached from Tirupattur, via Mattur, along Uttangari by a motorable road.

The area on the whole is a plain country, but the carbonatite outcrops at Sevathur and the fenites and syenites at Jokipatti are observed as tors 10 to 20 feet in height. Carbonatite outcrops in Jokipatti are very rare due to the soil cover of cultivated fields, and the vermiculite-pyroxene-fenites of Sevathur are also largely covered by soils. The soil cover is 2 to 3 feet in both cases and widely scattered fragments of magnetite 1 to 2 cm at Jokipatti and the micaceous soils at Sevathur indicated the presence of the rock types that had to be confirmed by test pits.

#### GEOLOGIC SETTING

The carbonatites of Sevathur, Jokipatti and the ring complex of Elagiri are all intrusive in the Dharwar gneissic complex. The faulted boundary of



the Dharwars with the charnockites south of the Palar river, referred to earlier, runs just east-south-east of Elagiri, Sevathur and Jokipatti.

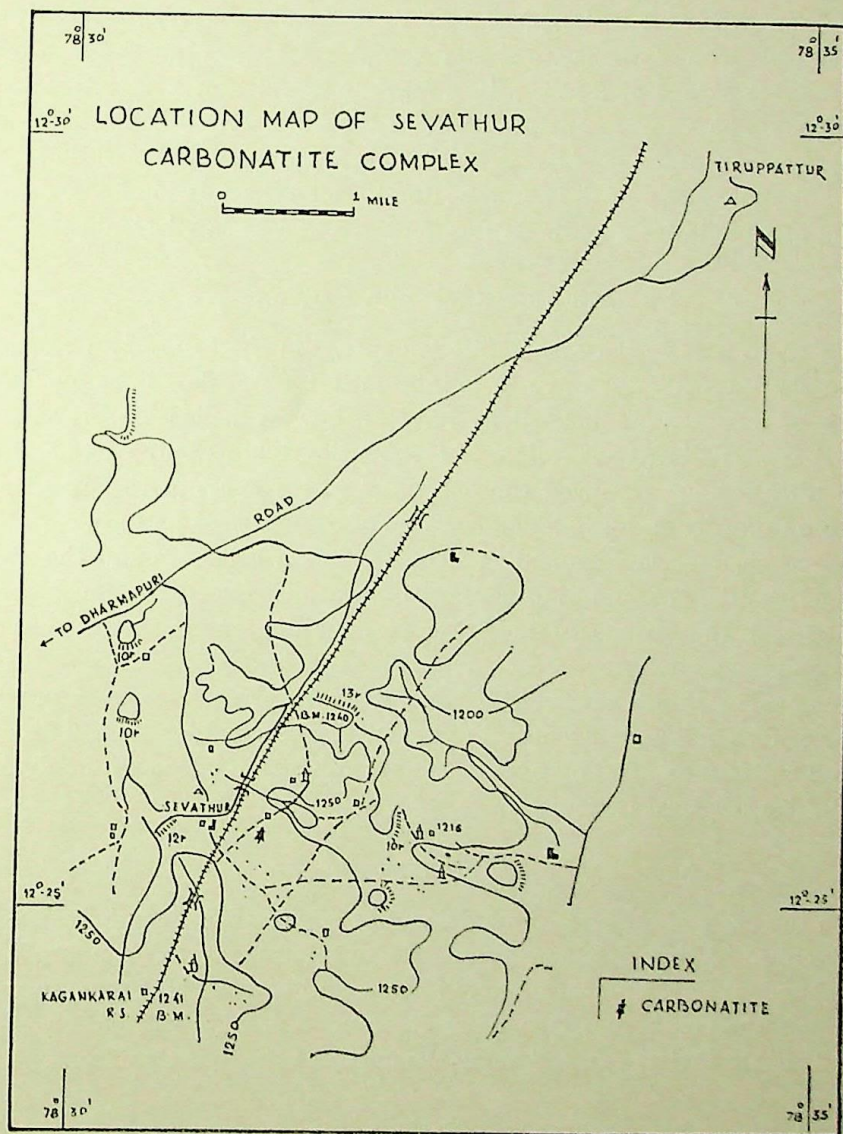


FIG. 1

The syenitic ring complex of Elagiri half a mile east of Jolarpet shows a wide circular rim about 800 to 1,200 feet high above the ground level. The ring has an outer diameter of 4 miles with a central depression that has a diameter of about 2 miles encircled by high hills of syenites 100 to 200 feet



high all around the inner rim. The breccias south-east of the rim are worked for barytes veins.

The carbonatites and syenites are situated along the east-north easterly line of fault within a distance of less than 2 km. west-north-west of the charnockites. The carbonatite fenite complex of Sevathur has an east-north easterly extent of 3 km. with a maximum width of 220 metres in the central part which tapers out gradually at the sides. At Jokipatti the total estimated extent of the complex is over 6.5 km. in length and a width of over 2 km., but the paucity of the outcrops due to soil cover has hindered detailed marking of boundaries of carbonatites, fenites and associated syenites.

#### STRUCTURE OF SEVATHUR CARBONATITE

The main part of the carbonatite is exposed in the form of an elongated crescent-shaped body intrusive in granite gneiss. The flow lines marked in portions of a soda amphibole sövite have an inward inclination towards the core. A few small arcuate collars of carbonatite dykes rarely exceeding five feet in thickness are arranged concentrically with respect of the main mass. These dip inwardly and give an appearance of a cone sheet pattern.

Felspathic breccia surrounding fenites forms a collar around the carbonatite. Inwards, the first ring consists of white sövites. The inner core is beforstic. A thin fringe of ankeritic carbonatite intervenes between the sövites and beforstite.

The evidence that carbonatites have acted as intrusive rocks is provided by the network of fine stringers and dykes cutting through fenites and breccias. The well cuttings exposed by excavation give an explicit view of the dykes of carbonatites bordered by fenites.

#### SÖVITES

On the basis of mineral composition, the sövites can be subdivided into four groups. Although these groups do not form mappable units in the field, abundant development of large (2 to 3 cm.) crystals of magnetite within and along the southern fringe of sövites and a scanty distribution of this mineral within sövites exposed along the northern fringe is significant.

##### (i) *Riebeckite-sövite and pyroxene-mica-sövite*

The sövite, of which calcite forms the chief constituent, shows typical flow structures due to oriented and elongated needles and laths of blue coloured riebeckite and brown coloured vermiculites. The crystals of apatite elongated in spindle shapes are arranged parallel to the flow lines. In linear parallelism to the flow lines are other minor constituents of the rock, namely magnetite, monazite and perovskite.



(ii) *Sövites consisting chiefly of calcite with only very small amounts of other constituents*

They have a width of 50 feet and extend along the entire length of carbonatite. These have practically very little of dolomite, with apatite and magnetite only as accessories. The calcite occurs as anhedral crystals up to 1 cm. across. These sövites are exposed along the southern contact of the carbonatite with the fenites.

(iii) *Magnetite-sövites*

The sövites exposed along the southern periphery are coarse-grained and are unusually rich in large crystals of magnetite. The magnetite crystals up to 8 cm. squares are abundant. The other major constituent is calcite. Apatite, monazite, calzirtite and zircon form the accessories.

(iv) *Sövites rich in apatite*

Sövites in general are poor in apatite but at their contact with ankerites show enrichment of apatite.

The contacts of sövites with them are not sharp but transitional. These merge gradually into ankerites and beforites. Although veins of ankerites and beforites in sövites are very common, sövites cutting across ankerites and beforites are never observed. Evidently the sövites appear to be the first phase of carbonatitic activity. Sövites at the contact are partly dolomitic, but there is no replacement relationship between calcite and dolomite, their contacts being sharp.

#### ANKERITIC CARBONATITE

This occurs as a thin fringe about 100 feet in thickness between the sövite and beforite. It is a brown coloured medium to fine-grained rock with small elongated crystals of buff coloured apatite, brown vermiculite and bluish dolomite with black siderite and rhodochrosite which give it a multi-colour shining lustre and flow lines to a freshly broken rock. In thin sections ferruginous matter along rhombic cleavages of carbonates is observed. This rock shows 4 to 8 times the background count on a portable gamma ray radiation counter in the field and analyses 0.04 to 0.08 per cent of  $U_3O_8$  equivalent. The radioactivity is due to uraniferous pyrochlore, monazite and cyrtolite variety of zircon.

Apart from the main fringe of the ankeritic carbonatite within the sövite there are numerous thin steeply inclined dykes and related sheets, veins and stringers which riddle the fenites and intrude the sövites.

#### BEFORSITE

Beforsitic carbonatite occupies the core of the carbonatite complex with a width of over 250 feet. It is a medium to coarse-grained buff coloured rock



with big crystals of magnetite. On weathered surfaces greenish crystals of apatite stand out prominently. Beforsite is made up entirely of dolomite with practically no calcite. Apatite is a major constituent besides magnetite. The radioactivity in beforsite is due to accessory monazite and uraniferous pyrochlore.

A band of about 1 foot in width and exposed over a length of 500 feet is rich in apatite. The apatite crystals here are 1 inch in length and stand out prominently (Fig. 2). A sample from this beforsitic carbonatite analysed  $P_2O_5 = 14.22$  per cent.

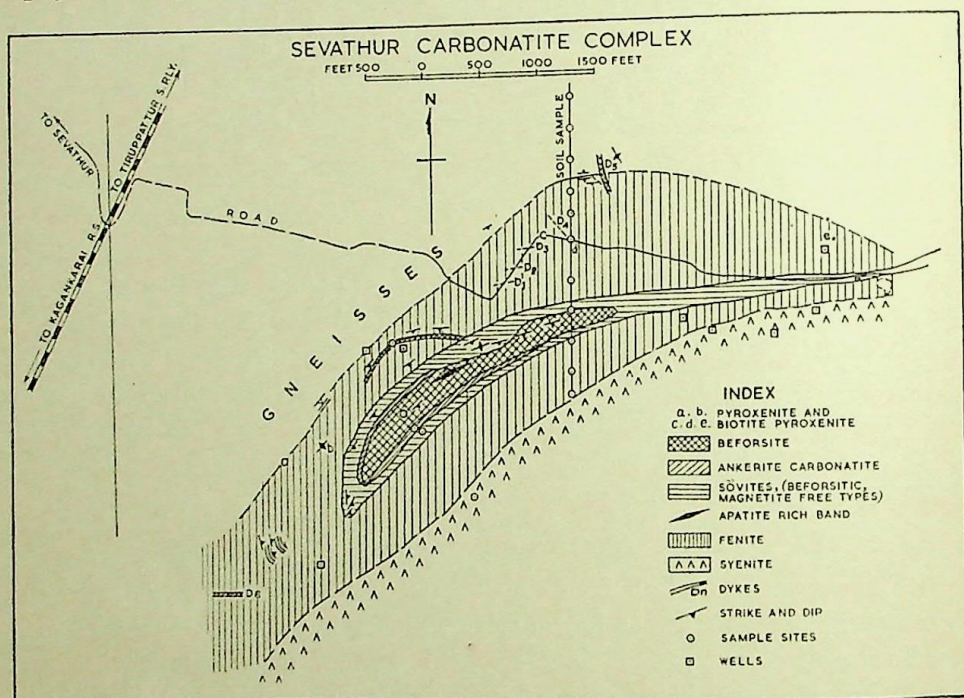


FIG. 2

$P_2O_5$  contents of rocks and soil samples along the north-south line and across the carbonatite at Sevathur are given in Table I.

Thin sections of the three types of carbonatites were stained by copper nitrate (Rodgers 1940) to compare the distribution of apatite with the calcite and dolomite in the carbonatites. Preferential concentration of apatite in dolomitic beforsites at Sevathur was significant. The soil samples on the average contain over 8 per cent of  $P_2O_5$  which can be raised easily by quenching magnetic and gravity separations. This area thus holds great prospect for a fertilizer industry in Madras State. Added to this, the presence of the carbonatite at Jokipatti in exactly a similar geological setting and identical mineralogy envisages an industrial proposition.



TABLE I

No.	Rock type	P <sub>2</sub> O <sub>5</sub>	Soil samples from north to south	*P <sub>2</sub> O <sub>5</sub> %
1	Vermiculite pyroxinito	3.47	I	8.62
2	Sövite	2.65	II	8.00
3	Ankerite	1.21	III	8.18
4	Sövitic beforosite	6.39	IV	11.00
5	Apatite rich beforosite	14.22	V	4.80
6	Beforsite	2.54	VI	10.50
7	Grey syenite	0.50	VII	6.38
			VIII	9.50
			IX	7.31
			X	4.00

\*After T. Deans (1967).

Note: Sample numbers refer to the sites in Fig. 2.

### FENITES

Fenites are mosaic in appearance riddled by veinlets and stringers of beforositic carbonatites. Concentric and radial dykes of carbonatites are traceable within fenites. Their thickness never exceeds five feet but several dykes about a foot in thickness are observed to cut across the fenites. Close to the carbonatitic matter within fenites, distribution of vermiculite rich pyroxenites is abundant. The pyroxenites form as screens between the minor arcuate collars of carbonatite and the leucocratic fenites. Pits put for recovery of vermiculite show some fresh outcrops of the rock type. The outcrops are highly weathered and friable grains of pyroxenes and books and flakes of vermiculite can be recognized megascopically. Thin sections of pyroxenites show granular aegirine augite with vermiculite, apatite and calcite as major constituents with magnetite, nepheline, anorthoclase as minor; and monazite and pyrochlore as accessories.

The shape of the aureole of fenitization here is nearly oval surrounding the carbonatite. The country rock involved consists mainly of the Dharwar gneissic complex that was granitic. Owing to the variety of rock types within the aureole and the cover of the soil topping the fenites it is not possible to delimit zones of fenitization except to record the fact that at the immediate proximity of the carbonatite dykes and where the veinlets of carbonatite are profuse vermiculite pyroxenite has developed.

The ultimate product of fenitization to the south is a syenitic rock consisting mainly of aegirine augite, orthoclase, microperthite, anorthoclase, sodic plagioclase and albite. The contact between the carbonatite and fenite is only inferred. In hand specimen the rock has a gneissic appearance due



to preferred orientation of the mafics and felspar laths about 1 inch in length. In thin sections quartz is seen to have been replaced by aegirine augite while the original felspar is altered to microperthite with striped appearance and finally to anorthoclase. The accessory minerals include magnetite, apatite, monazite and sphene, the last named being completely absent in the original gneisses. Occasional appearance of nepheline and analcite in some fenites is indicative of desilication and removal of silica from the otherwise quartz rich granite-gneisses. The fenites as a whole are microperthite-albite aegirine augite syenites.

#### SYENITES

A shonkinitic ring dyke borders the southern periphery of the carbonatite fenite complex mentioned above. The main rock type can be traced all along the length of the carbonatite. It is a coarse-grained rock with equal development of felsic and mafic minerals. In sections it consists of microperthite and albite, as felsics and amphibole, aegirine augite and biotite as mafic minerals. On the basis of colour index the rock could be grouped as ijolite, but is compared favourably with shonkinitic on the basis of the mineral assemblage. This rock type is nowhere exposed along the northern periphery of the carbonatite, except for a syenitic aplite dyke at the north-eastern side of the vermiculite pit. Accessory minerals of shonkinitic are monazite, apatite, zircon, perovskite, magnetite and calcite.

#### JOKIPATTI CARBONATITE

The carbonatite at Jokipatti has a setting and mineralogy identical with that of the Sevathur carbonatite. The significant presence of uranothorite observed at Jokipatti seems to be absent at Sevathur.

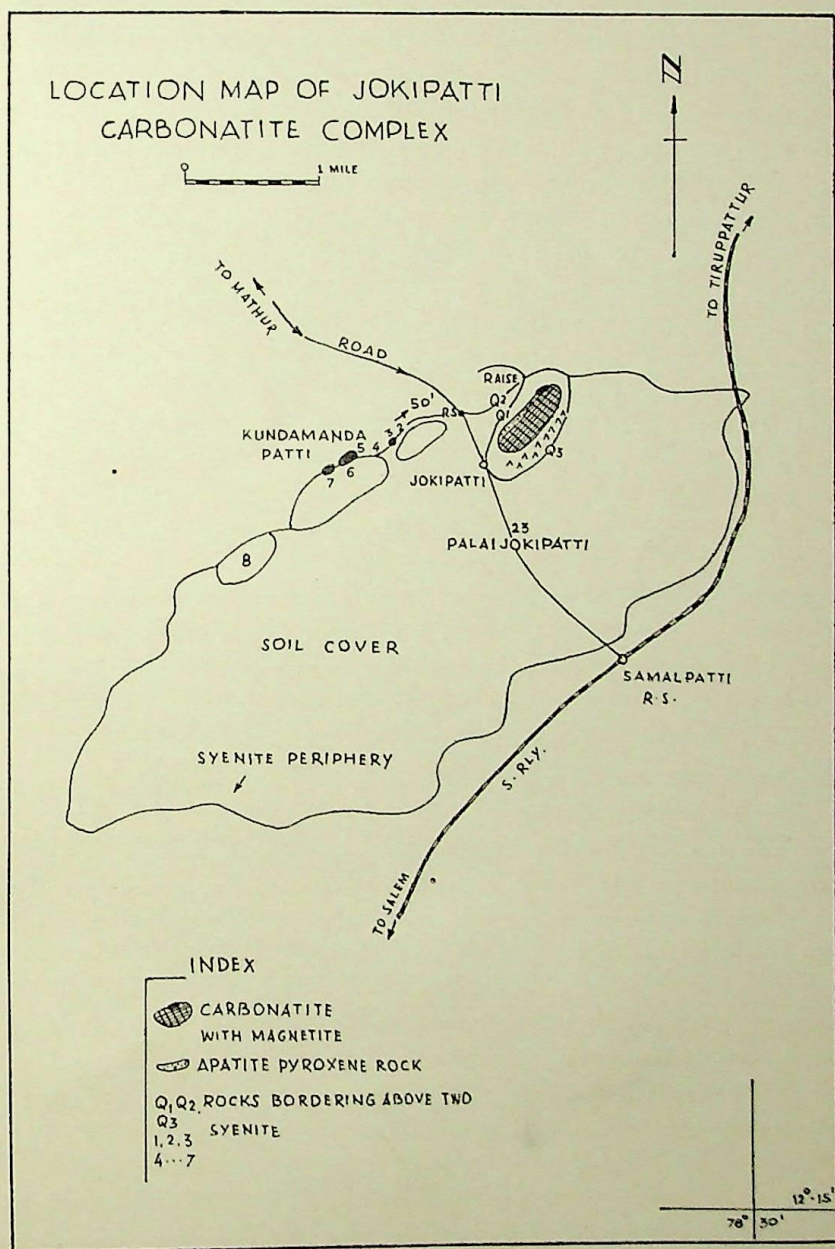
The carbonatite alkalic complex as a whole has an area of six square miles. It has an east-north easterly trend parallel to the shears marked by faulted contact of the charnockitic region with the Dharwars. The carbonatite body is intrusive in the Dharwar granite-gneisses.

Outcrops of the carbonatite are very scarce in the area, as these are covered by cultivated fields. Some outcrops, however, to the north-east of the village Jokipatti and south of the village Kundamanda are exposed to view along small hillocks bordered by fenites and syenites. In the cultivated fields wide and rich distribution of magnetite crystals serve as indicators of the carbonatite otherwise covered by scree and soil. The cover of the soil here is quite thick from 3 to 5 feet. A  $P_2O_5$  content of 2 to 5 per cent from soils at depth was observed.

The contact of the carbonatite and fenite to the south of the region is not exposed, but the syenite-granite boundary as marked on the map (Fig. 3) serves the delimiting horizon of the complex.



The mineralogy and zoning in this complex is similar to Sevathur, with a difference that uranothorite is the additional radioactive mineral and



monazite, pyrochlore and zircon content in the fenites here is more as compared to the Sevathur fenites. The syenites of the complex are exposed



prominently to the north as well as to the south and form a ring around the carbonatite complex. The syenites are rich in amphibole riebeckite-richterite with subordinate amount of aegirine. The feldspars which constitute the major constituent are microperthite and albite, nepheline as well as free quartz are absent.

#### GEOCHEMISTRY

The most significant guiding factor that has proved useful in the field is the radioactivity of the carbonatites. The ankerites and beforites showed  $4\frac{1}{2}$  times the background count on portable radiation Geiger Muller Counters, whereas the sövites recorded  $1\frac{1}{2}$  to 2 times the background count. The  $U_3O_8$  equivalents varied from 0.01 to 0.04 per cent at Sevathur and 0.02 to 0.2 per cent at Jokipatti. Separation of radioactive minerals has shown the presence of monazite, pyrochlore, fersmite and zircon at Sevathur and uranothorite, monazite and pyrochlore at Jokipatti.

Table II gives the analyses in per cent of the samples analysed at the Institute of Geological Sciences, U.K.

TABLE II  
*Analyses in per cent*

Sl. No.	Samples Sevathur area	Sr	Ba	y	La	Ce	Nb	$eTh_2^0$	$^{87}Sr/^{86}Sr$
1	Sövite	0.70	0.13	0.006	0.03	0.04	Nil	n.a.	0.7053
2	Beforsite	0.75	0.06	Nil	0.02	0.01	0.002	n.a.	0.7057
3	Pyroxenite soil	0.06	n.d.	0.005	n.a.	n.a.	0.002	0.005	n.a.
4	Alkali ambhibole sövite	0.91	0.12	0.005	0.03	n.a.	n.d.	tr.	n.a.
5	Beforsitic sövite	0.85	0.09	0.005	0.03	n.a.	n.d.	tr.	n.a.
6	Magnetite sövite	1.10	0.09	0.010	0.02	n.a.	n.d.	n.d.	n.a.
7	Ankerite soil	0.08	0.06	0.005	0.20	0.20	2.20	0.13	n.a.
8	Beforsite	1.23	0.06	n.d.	0.01	n.a.	tr.	0.005	n.a.
9	Ankerite	0.76	0.16	0.005	n.a.	n.a.	n.d.	0.004	n.a.
10	Sövite of *Jokipatti	1.00	0.80	0.01	0.03	n.d.	0.002	n.a.	n.a.

Note:

1. n.d. → not detected.
2. n.a. → not determined.
3. tr. → Traces.

\* Samples from Jokipatti.

#### DISCUSSION OF RESULTS

The carbonate rocks examined agree favourably with the known carbonatites in respect of both trace elements and mineralogy. Notable is the abundance of strontium and the enrichment of barium and lanthanum-cerium rare earths. Presence of apatite, magnetite, monazite and alkali amphiboles and pyroxenes in these carbonate rocks is characteristic.



From sample number seven the rare mineral Fersmite ( $\text{Ca TR}$ )  $\text{Nb}_2\text{O}_6$  was identified by X-ray. This mineral is known elsewhere in three different associations (i) Vyahnyevye Hills (Urals, U.S.S.R.) in alkali syenite complex (with subordinate carbonatites), (ii) with columbite in Ravalli country, Montana, U.S.A., and (iii) as microscopic inclusions in pyrochlore in several carbonatite complexes (Panda hill, Tanzania; Söva, Norway; Lueshe, Congo; East Siberia, etc.).

In mineralogy and trace elements the Sevathur and Jokipatti carbonatite complexes are comparable with occurrences in Ravalli County, Montana, U.S.A.

Individually high contents of phosphorus, strontium and barium cannot be regarded as characteristic of carbonatites but collectively enrichment of P, Sr, Ba, La, Ce, and Nb are usually regarded as diagnostic. Yttrium is notably less enriched in carbonatites than lanthanum and cerium.

In recent years the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios have come to be considered as an additional tool to determine the primary nature of materials derived from below the earth's crust. The isotope ratios of  $^{87}\text{Sr}/^{86}\text{Sr}$  in carbonatites vary from 0.703 to 0.706. The mean average of 0.7055 for Sevathur carbonatite gives additional proof that these are true carbonatites.

#### GUIDE LINES FOR FURTHER RESEARCH

Having described the two complexes in some detail, it may be interesting to discuss the regional geological setting of these. This discussion may lead to the discovery of other areas where carbonatite rocks in the southern shield are postulated and could be worked out.

The carbonatite complexes at Sevathur and Jokipatti have a east-north easterly elongation parallel to the Palar river fault (Fermor 1936). The rocks south of Palar are charnockites whereas to the north acid granites are found (Pascoe 1926).

From the considerations of (i) orographical map of India, (ii) greater susceptibility of charnockitic region shown in the seismic sketch map, (iii) absence of Purana rock in the charnockitic region and (iv) the hypometamorphic impress preserved in the charnockites, Fermor (1936) postulated the uplift of the charnockitic region with respect to the non-charnockitic regions. Although later workers have been able to show that charnockites have locally transgressed the boundary originally postulated by Fermor, Radhakrishna (1968) has produced convincing evidence to indicate that 'the present position of charnockites is a result of faulting and repeated uplift'.

Several shear zones parallel to the main boundary of the Dharwars with charnockites are under investigation for search of radioactive minerals by the Atomic Minerals Division. In view of the significant location of carbonatitic rocks and alkali syenites along this line of fault, it is proposed to search for more occurrences of carbonatites and alkalic rocks.



Peridotites, eclogites and corundum-syenites of Salem, Sivamalai and Coimbatore to the south-east of the complex and peridotites of Baster, M.P., nepheline-syenites, pyroxenites and gabbros with norites in Baharguda and Poduguda in Koraput district of Orissa towards the north-east and their vicinities need to be searched for possible localities of carbonatites.

Agglomerates traversed by calcite veins are mentioned (Pichamuthu 1935) in the vicinity of the Wajrakarur kimberlite. Sen and N. Rao (1967) report a possible carbonatite occurrence of Chelima in Nallamala range. The latter is apparently genetically related to the kimberlite and is being prospected for lead, zinc and copper by the Geological Survey of India. Gangue of barite, dolomite, calcite, etc., suggest a possibility of radioactive minerals being associated with the complex at Chelima. Wajrakarur and Chelima open a possibility of further search of carbonatites along the margins of the Cuddapah basin, which is possibly deposited along a rift valley (Dar 1964).

The K/Ar ages for pyroxenites in Sevathur were estimated at  $720 \pm 30$  million years. The age for Elagiri syenites was determined as  $770 \pm 30$  million years. These age determinations indicate that the carbonatite alkalic complexes are much younger than the Dharwars as well as the charnockites. The close age relationship of intrusive alkalic complexes and the charnockite uplift cannot be ruled out.

The carbonatite alkalic rock complexes and their relation to kimberlites as available in the southern peninsula is not only of vital interest to fundamental research on carbonatites but is also another approach to solve the century-old controversy about the space and time relationship of the charnockitic uplift of the southern plateau. Rich deposits of phosphates and other minerals of which carbonatites are repositories enhance the attraction of this problem.

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#### DISCUSSIONS

*Questioner's Name: Dr. D. N. Wadia*

*Question:*

Is the author convinced about the magmatic origin of Indian carbonatite?

*Author's Reply:*

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.7055 of the Sevathur carbonatite correlates it with the rocks of magmatic origin.

*Questioner's Name: A. V. Sankaran*

*Question:*

(1) The *Nb* content in some of the carbonatite suite of rocks show *Nb*—0.002%, which is not any higher than crustal average given out by many authors.

(2) The *La* content of some of the samples are greater than *Ce* is against Oddo-Harkins rule.

(3) Can he comment on the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio pointing to the same origin?

*Author's Reply:*

(1) The content of *Nb* varies from 0.002 to 2.1%.

(2) Enrichment of *La* and *Ce* over *Y* is a characteristic of carbonatites.

(3)  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of samples from Sevathur give an average value of 0.7055.

*Questioner's Name: Bhattacharyy, T. K.*

*Question:*

(1) What are the textural variations, mineralogical changes and chemical variations? What are the sequencies of metasomatism based on the above from parent rock to the final produce?

*Author's Reply:*

The variations show the rock types from vermiculite pyroxenites to ijolites to nepheline syenites and syenites all after alteration of granitic gneisses.



## FLOTATION OF BERYL FROM BERYL DUST

by V. M. KARVE and K. K. MAJUMDAR, *Ore Dressing Section, Metallurgy Division, Bhabha Atomic Research Centre, Bombay 85 (AS)*

(Received 29 April 1969)

A simplified procedure has been developed for the beneficiation of beryl dust from Doddakadanur, Mysore State (BeO content 3 per cent), from its associated minerals. The mineralogical composition of the dust was: beryl 24 per cent, feldspar 35 per cent, quartz 33 per cent, apatite 4 per cent, mica 2 per cent and others 2 per cent. The ground feed was deslimed and then conditioned with a mixture of sulphuric and hydrofluoric acids for the removal of  $\text{Fe}^{+++}$  and activation of beryl. The excess acid was removed by thorough washing. This was followed by flotation with sodium oleate at natural pH. The concentrate was cleaned twice by flotation. The final concentrate assayed 10 per cent BeO, the recovery being 85 per cent. This is expected to be more than 90 per cent on recirculation of recleaner tails.

The above procedure is an improvement over the procedure developed in our laboratory earlier, when the flotation with sodium oleate was carried out at pH 3 necessitating use of sulphuric acid for pH adjustment. The consumption of sodium oleate was high as a large amount of the collector was thrown out at this pH.

### INTRODUCTION

Several workers have studied the concentration of beryl from the low grade ores. Because of the fact that the associated minerals have more or less similar physical properties, only flotation has been successful so far in beneficiation of beryl. From the work of many workers in the field, four procedures have emerged. These are described below in short:

(1) Eigeles process (Eigeles and Levush 1958) consists essentially in conditioning the cold, ground and deslimed pulp at 50 per cent solids with 1.5–2.0 kg/tonne of sodium sulphide, then raising the temperature to 80–85 °C and adding 0.2–0.4 kg/tonne of oleic acid. The pulp is then diluted and the beryl concentrate floated.

(2) Lamb's technique (Lamb 1947) consists in conditioning the ground and deslimed ore with about 2 kg/tonne of hydrofluoric acid (HF), then washing thoroughly and floating beryl with oleic acid (O.A.) and fuel oil.

(3) In Runke's method (Runke 1954) mica is first removed using tallow amine acetate at pH 3.5. Beryl is then floated with petroleum sulphonate (P.S.) at pH 2.2.

(4) In Rapid City process (Runke 1954) mica is removed by flotation using amine collector at pH 3.5. A combined float of beryl and feldspar is then obtained by adding HF and more amine. The amine coating on the



bulk concentrate is destroyed by conditioning with hypochlorite. After thorough wash beryl is floated with P.S. at pH 2.5.

From the above it can be noted that the Eigeles process is having a drawback in that the whole pulp has to be heated to 80–85 °C. Runke and Rapid City procedures give two or more products and the flotation pH is as low as 2.5, which entails additional difficulties in operation. Lamb's procedure is comparatively simple and gives only one product.

The effect of the inorganic ions like Ca, Mg, Fe and Al on the flotation of pure beryl and associated gangue minerals, viz. quartz and feldspar, was studied in this laboratory (Viswanathan *et al.* 1965). Sodium oleate (Na-OL) was used as the collector. It was noted that the flotation of beryl is Fe sensitive and it is possible to get a high grade beryl float only in the absence of ferric ions. Ca and Mg ions did not interfere if the pH was maintained between 3 and 6.

Based on these observations on the pure minerals a flotation process was developed for a low grade beryl ore from Doddakadanur, Mysore State (Karve *et al. in press*). The process is briefly described below: The ore is ground to –35 mesh and thoroughly deslimed. The deslimed ore is scrubbed at a high pulp density (p.d.) to remove some more slimes. The ore is then treated with caustic soda, sulphuric acid ( $H_2SO_4$ ) and HF in stages and finally floated at around pH 3 with Na-OL.

The procedure outlined above is a multistage operation and hence complicated. As the pH of flotation is on the acidic side, a good amount of collector is needed and the flotation is rather slow.

Recently a beryl dust sample was received from Doddakadanur, Mysore State, for beneficiation testing. The procedure mentioned above, developed in this laboratory, was re-examined in the light of Lamb's comparatively simple procedure and encouraging results were obtained.

#### MATERIALS AND METHODS

The beryl dust received was in two sizes, one coarse ( $\frac{1}{4}$ ") and the other fine (10 mesh). The mineralogical composition of the samples was more or less similar and that of the coarse sample is given below: beryl 24 per cent, feldspar 35 per cent, quartz 33 per cent, apatite 4 per cent, mica 2 per cent and others 2 per cent. On chemical analysis the sample assayed 3.0 per cent BeO. The coarse sample was first taken up for the beneficiation tests. The microscopic examination of the ground product revealed that beryl liberated at coarse size and hence the ore was ground to pass through 35 mesh. Laboratory Fagergren cell with a stainless steel bowl was used for the flotation tests. Na-OL was used as the collector. All the chemicals used were of C.P. grade.



## EXPERIMENT AND RESULTS

The ore was ground in a laboratory rod mill (8"×14") with 6.5 kg of rods ( $\frac{1}{2}$ "– $\frac{3}{4}$ " dia×12"). 1.5 kg of the ore was taken at a time with one litre of water. The grinding time was varied from 5 to 20 minutes. 20 minutes grinding time was found to be suitable as most of the ground product passed through 35 mesh. The percentage of –200 mesh fraction in the ground feed was 20.4.

The ground product was wet sieved through 35 mesh and the +35 mesh fraction was fed back with new feed in the next grinding. The –35 mesh fraction was thoroughly deslimed before any flotation test was carried out. Stainless steel buckets were used for desliming. After carrying out a number of such desliming operations, it was found that the slimes were 9–10 per cent by weight and the loss of beryl amounted to 5–6 per cent in this fraction.

From the previous experience on a similar ore it was known that a pretreatment with acid was a necessity and HF was found to be the most efficient in cleaning the surface of the minerals. To arrive at the minimum amount of the collector that should be used, initially a large amount of HF was used for the pretreatment. The flotation procedure adopted for the testing was as follows: The deslimed feed was conditioned with known amount of HF for 10 minutes. The solids were allowed to settle and the supernatant liquid decanted off. The solids were repulped, churned for 2 minutes, allowed to settle and decanted. The procedure was repeated three more times. The feed was then conditioned with a known amount of Na-Oleate for 3 minutes at about 40 per cent solids, diluted to about 20 per cent solids and floated at neutral pH (about 7). No frother was used. The float was cleaned twice without adding any further reagents.

To start with 15 kg/tonne HF was used for the pretreatment and Na-Ol was varied from 0.2 to 0.7 kg/tonne. It was found that at least 0.4 kg/tonne Na-Ol was essential for the complete flotation of beryl.

After finding the minimum amount of the collector, the quantity of HF used for the pretreatment of the feed was varied from 15.0 to 0.5 kg/tonne in suitable stages. It was observed that to get tailings almost free of beryl a minimum of 2.5 kg/tonne HF was needed.

In the procedure fixed for finding out the minimum amount of acid for the pretreatment and the minimum amount of collector, the conditioning time with the acid was fixed arbitrarily as 10 minutes. This was then varied from 10 to 5, 3, 2 and 1 minutes. There was not much variation in the results obtained. Hence, the conditioning time with HF was fixed as 2 minutes for further work.

During the course of the work it was noted that after the acid conditioning it was absolutely essential to wash the feed free of acid prior to flotation.



If some acid was left in the flotation circuit, the frothing characteristics of the collector were affected to a great extent. The froth proved to be brittle and the flotation time was increased. In the next phase of the work, therefore, this aspect was studied. It was found that the feed must be washed at least three times before the addition of the collector. In a few trials instead of washing the feed free of acid, after conditioning, the acid was neutralized with alkali. But in such cases no froth could be obtained.

The results of a typical flotation test, on employing the optimum conditions discussed above, are given in Table I.

TABLE I  
*Beryl Flotation Using HF for Pretreatment*

Product	% Wt.	% BeO	% Dist. BeO
Slimes	8.7	2.0	5.3
Rougher tails	48.4	tr	—
Cleaner tails	11.6	0.4	1.6
Recleaner tails	5.0	5.0	7.8
Recleaner conc.	26.3	10.3	85.3
Calc. head	100.0	3.19	100.0

From the above table it can be seen that major loss of BeO takes place in the recleaner tails which, in any case, could be recirculated in a continuous operation.

HF is 15–20 times as costly as  $H_2SO_4$ . Experiments were carried out to see whether  $H_2SO_4$  or hydrochloric acid (HCl) could replace HF. It was observed that the recovery of beryl in the rougher float amounted to only 80 per cent in such cases as against almost complete recovery when HF was

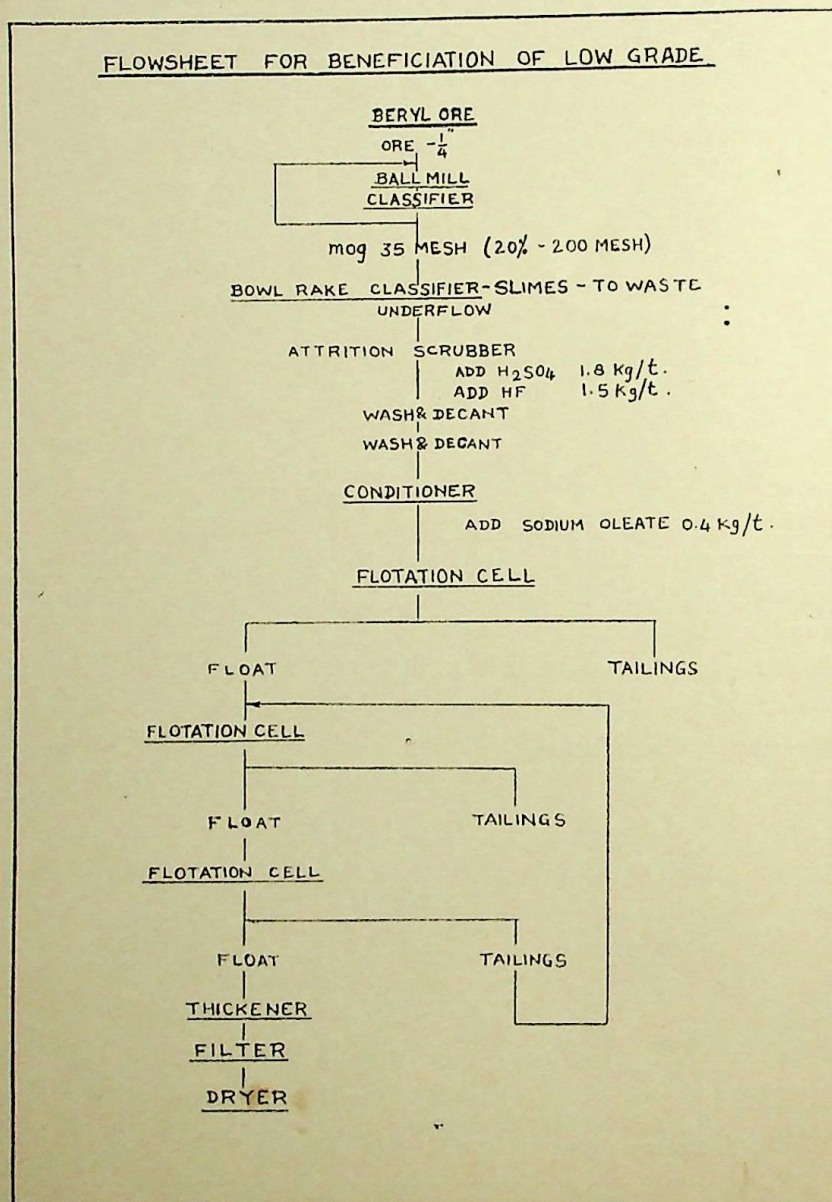
TABLE II  
*Beryl Flotation Using a Mixture of HF and  $H_2SO_4$  for the Pretreatment*

Product	% Wt.	% BeO	% Dist. BeO
Slimes	9.0	1.8	5.2
Rougher tails	49.0	tr	—
Cleaner tails	12.2	0.9	3.5
Recleaner tails	3.4	6.4	7.0
Recleaner conc.	26.4	10.0	84.3
Calc. head	100.0	3.13	100.0



used. The flotation was comparatively slow and finished product of required BeO assay (10 per cent BeO) could not be obtained. This clearly indicated that HF is not only efficient in cleaning the surface of the minerals but also is an activator for beryl.

The work was therefore continued using a mixture of HF and  $H_2SO_4$  for the pretreatment. Using excess of  $H_2SO_4$ , the minimum amount of HF that





must be used for the complete flotation of beryl was determined. Keeping this minimum amount of HF constant, the proportion of  $H_2SO_4$  was varied. These experiments showed that the HF consumption can be brought down from 2.5 to 1.5 kg/tonne if used along with 1.8 kg/tonne  $H_2SO_4$ . The difference in the cost of the two acids being considerable, the combination of acids should be preferred. The results on employing the acid-mixture for the pretreatment are incorporated in Table II.

The conditions established above for the coarse sample were found to be equally good for the finer sample of the ore. Only the grinding time had to be changed from 20 minutes to 10 minutes.

Based on the above studies a flowsheet has been suggested for the beneficiation of beryl dust (Fig. 1).

### CONCLUSIONS

(1) In the earlier paper on the beneficiation of a low grade beryl ore, a number of stages were suggested for the pretreatment of the ore. On re-examining the procedure it was found that desliming and single stage acid conditioning is quite adequate.

(2) The consumption of HF, a costly reagent, can be brought down if a mixture of HF and  $H_2SO_4$  is used.

(3) The flotation, when carried out at neutral pH (about 7), is faster and the amount of collector could be brought down to less than half of what is required if the flotation pH is maintained on the acidic side.

### ACKNOWLEDGEMENTS

The authors' thanks are due to Shri N. K. Rao, for carrying out mineralogical analysis and to the analytical chemistry group for the chemical assay of the products. The authors are thankful to Dr. V. K. Moorthy, Head, Metallurgy Division, for his interest in the problem.

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# PROCEEDINGS OF THE INDIAN NATIONAL SCIENCE ACADEMY

No 5

September 1970

Vol 36

## CONTENTS

	<i>Page</i>
Studies in the Beneficiation of Uranium Minerals from Narwapahar— Singhbhum <i>by</i> C. GHOSH, J. B. NARASIMHAM <i>and</i> K. K. MAJUMDAR ..	285
Some Results of Lixiviation Tests on Bulk Uraniferous Quartzite Ore under Field Conditions at Chhinjra, Kulu District, Himachal Pradesh <i>by</i> K. M. V. JAYARAM <i>and</i> S. C. KULSHRESTHA .. .. .	291
Leaching and Precipitation of Uranium from Quartzite Ores at Chhinjra, Kulu District, Himachal Pradesh <i>by</i> K. M. V. JAYARAM, A. S. DESH- PANDE <i>and</i> C. V. SHARMA .. .. .	298
Extraction and Utilization of Pure Niobium and Tantalum from Indian Ores <i>by</i> A. D. DAMODARAN, S. G. DESHPANDE, A. A. MAJUMDAR, M. S. SASTRI, P. K. JENA, D. K. BOSE, S. CHANDRA, C. K. GUPTA <i>and</i> A. K. TANEJA .. .. .	306
Some Observations on Uranium-Copper Relationship in the Surda Copper Mines and their bearing on the Zoning of Mineralization in the Singh- bhum Thrust Belt, Bihar <i>by</i> K. K. SHARMA .. .. .	319
Carbonatites of Sevathur and Jokipatti, Madras State, India <i>by</i> G. R. UDAS <i>and</i> P. KRISHNAMURTHY .. .. .	331
Flotation of Beryl from Beryl Dust <i>by</i> V. M. KARVE <i>and</i> K. K. MAJUMDAR	344